TWO EARLY CHINESE BRONZE WEAPONS WITH METEORITIC IRON BLADES

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Two Chinese early Chou bronze weapons with iron blades.
Upper: *ko* 34.11, lower: *ch'i* 34.10. Slightly reduced.

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FOREWORD

The presence of iron blades in these two early Chou bronze weapons intrigued the late Archibald Gibson Wenley from the time he began to study them while working on the first catalogue of Freer Chinese bronzes that came out in 1946. In 1950 he asked the late Dr. William F. Foshag of the Department of Geology, Smithsonian Institution, to examine them from the scientific point of view; and the results of that investigation gave further stimulus to the founding of the Freer Technical Laboratory which was then in the planning stage and which was to open the following year under the direction of Rutherford John Gettens.

In spite of the calls for help that flooded the new laboratory from every side, Mr. Gettens returned to these two weapons from time to time; and during the ten years when the study of the ceremonial vessels was in progress much additional related information came to light. Roy S. Clarke, Jr. of the Division of Meteorites, Smithsonian Institution, and W. T. Chase, Assistant Curator of our laboratory and now Mr. Gettens's successor as its director, made important contributions at every stage of the work; and in recognition of this the book is published as the collaborative work of the three authors.

We are pleased at long last to publish this small volume, and it is only fair to point out that its size is in no way related to the immense amount of work that went into it. It should shed new light on the knowledge of metal technology in ancient China and also on other phases of the cultural history of that country some 3,000 years ago.

Freer Gallery of Art
Washington, D. C.
October, 1970

John Alexander Pope
Director

PREFACE

The authors are grateful to a number of persons who have helped in this study. First to Daniel Polansky and associates at the U.S. Naval Ordnance Laboratory, White Oak, Maryland for the radiographs which gave major impetus to the study in its early stages. Mrs. Elisabeth West FitzHugh made some of the bronze analyses and did much of the early X-ray diffraction work. Mrs. Ilona V. Bene also contributed to the chemical analyses. Dr. Michael B. Duke of the U.S. Geological Survey made the early electron microprobe exploratory studies. Joseph Nelen of the Division of Meteorites of the National Museum of Natural History obtained all of the electron microprobe data reported here. Dr. Kurt Fredriksson, also of the Division of Meteorites, gave valuable advice in connection with the probe work. Professor Paul Ramdohr of the University of Heidelberg, a specialist in ore microscopy, studied the polished sections of the two weapons. Dr. Joseph I. Goldstein of Lehigh University also participated in the discussions and contributed ideas.

Several have generously read the manuscript and made constructive comment: Dr. V. F. Buchwald of the Technical University, Copenhagen; Dr. Brian Mason of the Department of Mineral Sciences and Robert M. Organ of the Conservation-Analytical Laboratory, Smithsonian Institution; Dr. Cyril S. Smith of the Massachusetts Institute of Technology; and Dr. Thomas Lawton of the Freer Gallery. Grover Moreland, also of the Department of Mineral Sciences, prepared the metallographic mounts used in the study of the dagger axe. We are grateful to Raymond Schwartz of the Freer Gallery for much of the fine photographic work, and to Harold Westley of the Conservation-Analytical Laboratory, U.S. National Museum, for most of the spectrographic data presented here. The fact that this book has come out at all is in no small measure due to the patience and skill of our Editor, Lloyd E. Langford, who supervised every detail of preparing it for the printer and seeing it through the press.

The study was partially supported by NASA Grant NsG-688.

Rutherford J. Gettens
Roy S. Clarke, Jr.
W. T. Chase

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I. INTRODUCTION

The Freer Gallery of Art owns two unique metal weapons from ancient China (*frontispiece*). Though they have rarely been exhibited these weapons are shown in the old Freer catalogue (Freer Gallery of Art, 1946). One (34.10) is a broad axe (*ch'i*) with a bronze tang (*nei*) and the rusted remains of an iron blade; the other (34.11) is a dagger axe (*ko*) with a bronze blade and the remains of an iron point. Both were acquired in 1934 during the directorship of John Ellerton Lodge as part of a group of 12 bronze weapons said to have been found in 1931 in Honan province in China and to date from the early Chou dynasty (about 1000 B.C.). These two weapons are of high interest to the historian of technology for three reasons: (1) the combination of two different metals, one common at the time of manufacture and the other presumably unknown in China; (2) evidence that the two metals were joined by the casting-on method, a well-known technique of the Bronze Age in China; and (3) evidence that the iron in both weapons is of meteoritic origin.

Much of the information which points to the above conclusions comes from the use of a variety of instrumental techniques which in recent years have been widely applied to problems of art and archaeology: X-radiography, X-ray diffraction, electron-beam micro-spectrometry and emission spectrometry were all employed. The evidence from each technique will be introduced in its proper place. First, however, we must consider briefly the provenance, date and use of these two objects and describe them; a more complete discussion of the art historical questions these weapons raise and their place in the history of Chinese technology appears below in Section V.

Both weapons are well-known types and they can now be dated to about 1000 B.C. Magdalene von Dewall (1967, p. 527) dates them in the tenth century B.C. — very soon after the Chou conquest. Max Loehr (1956, p. 209) illustrates and describes several Shang or early Chou all-bronze broad axes of similar style

and shape to our *ch'i* (*yüeh*), and also several weapons in the style of our *ko*. Most are solid bronze but a few have jade blades; none of early date shown by Loehr have iron blades or points except a pair of bronze axes provisionally dated 770–450 B.C. with remains of iron pikes that look like handles. The kind of iron is not mentioned. There is scattered mention, however, of contemporary Luristan and Scythian swords with iron blades.

It might be presumed that the iron blades were attached to the weapons to make them more functional, but because of the scarcity of iron in the early Chou period, and the decor on the weapons, especially the inlay on the *ch'i*, it seems they were probably made for ceremonial purposes.

II. THE BROAD AXE (*CH'I*) 34.10

The object (*fig. 1*), which is 17.1 cm. long and 10.8 cm. wide, weighs 437.5 grams. The upper part of the blade and the tang (*nei*) is of a single piece of bronze; the blade or cutting edge is iron which was originally fashioned so that it could be secured in the edge of the bronze. The iron blade is apparently completely converted to rust (*fig. 2*) and has broken away from the tang. In the center part of the bronze axe head is a hole 1.8 cm. in diameter; and around this is cast, in narrow sunken lines, a stylized dragon form with eyes in low relief. In the end of the tang is also cast a *t'ao t'ieh* mask in relief with deep channels which apparently were originally inlaid with tesserae of reddish-brown material of which only tiny fragments still remain (see below). Two lashing slots in the back probably received thongs for hafting and a small "splint hole" in the tang may have held a transverse pin to help fasten the lashing. The bronze surface is mostly covered with blue and green copper corrosion products but in some areas, especially that part which was protected by the haft, the original polished metal surface still shows. The iron blade appears to be a complete mass of iron rust.

The bronze tang is cast in one piece, probably in a two-piece mold. Mold marks show distinctly along the upper edges of the broad head and at the corners where the tang joins the head (*fig. 3*). There are no mold marks on the inside of the smaller hole or on the inside of the two slots. These appear to have been drilled or cut in the bronze but it is also possible that they were cast. The sides of the large hole are concave. The long recess or slot to fit the iron blade appears to be cast in; the slot is still partially filled with iron rust and in the radiograph (*fig. 5*, see below) the irregular mottled area shown between edge and hole indicates the slot is about 1.5 cm. deep.

Samples for analysis were taken by hand drilling into the edge of the tang with a No. 44 (.086 inch) steel twist drill. After sampling the drill hole was plugged with threaded copper wire and

FIG. 1.—34.10. Two views of a Chinese bronze broad axe with iron blade of the type *ch'i* formerly inlaid; dated early Chou dynasty which began in 1027 B.C. It is said to have been dug up with other ancient weapons by a native at Hsün Hsien, Wei-hui-fu, Honan province, not far from An-yang district. Length, 17.1 cm.

the location of the spot concealed. Wet analysis for major constituents shows:

Cu	81.8 % (electrolytic)
Sn	15.8 % (gravimetric)
Pb	trace
Total	97.6 %

The analysis is the average of duplicate determinations made on samples weighing approximately 80 milligrams each (0.08 grams; see also Table 5 a).

Spectrographic analysis to estimate minor and trace constituents was carried out on a Jarrell-Ash 3 m. grating spectrograph. The analysis made on duplicate 10 mg. samples of bronze taken from the core shows, in addition to copper and tin, the following elements:

In the range	0.01–0.1 %	Bi, Fe, Ni, Sb, Si, Pb
In the range	0.001–0.01 %	Ag, Co
Less than	0.001 %	Cr, Mg
Sought but not found		Al, As, Mn, Zn

Metallographic structure of the bronze

No attempt was made to take a section of the bronze for metallographic polishing and etching. Scattered areas of the surface are not encrusted with corrosion products but are still metallic in appearance. Examination at ×30 magnification shows, however, that corrosion has begun in these areas sufficiently to etch the metal and to reveal its crystalline structure. The darker dendritic forms of high-copper low-tin alpha bronze stand out against the lighter areas of tin-rich alpha which have been partially corroded, probably to hydrous tin oxide, H_2SnO_3 (*fig. 4*). This is clear evidence within the metal itself that it was formed by casting.

FIG. 2.—34.10. Chinese bronze broad axe of the type *ch'i* with iron blade. End view (× 2) showing laminated structure of the iron rust retained inside the bronze ferrule.

FIG. 3.—34.10. Chinese bronze broad axe of the type *ch'i* with iron blade. Detail (× 1.7) showing a ridge along edge of the tang which is the flash (mold mark) left at the juncture of the two halves of the mold in which the axe was cast.

Corrosion products

Much of the bronze surface is thinly encrusted with malachite, $Cu_2(OH)_2CO_3$, and azurite, $Cu_3(OH)_2(CO_3)_2$. The edge of the break across the middle reveals that in places the metal is penetrated clear through with cuprite, Cu_2O.

Some fragments of wood are still attached to the edge of the iron (*fig. 1*). The wood could not be identified because it is so rotted that no diagnostic features remain; not even enough to identify the class of wood.

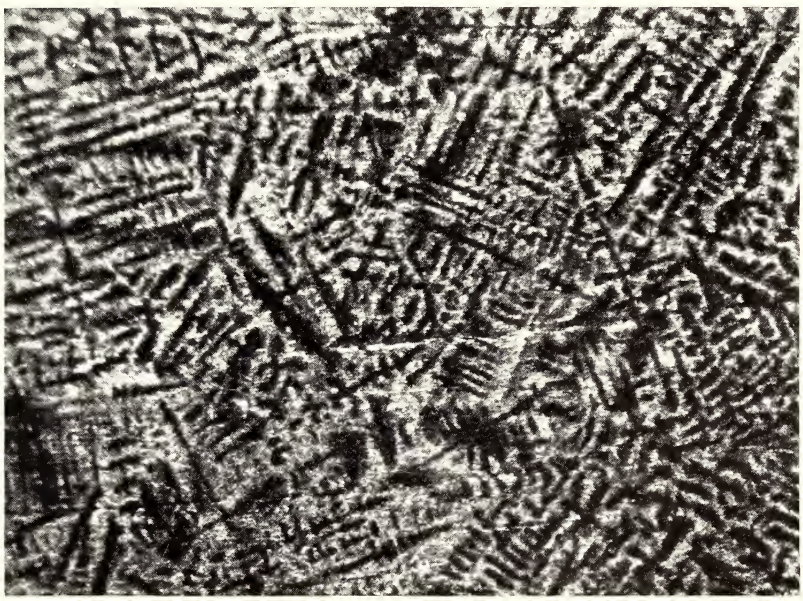

FIG. 4.—34.10. Chinese bronze broad axe of the type *ch'i* with iron blade. Metallograph (×75) of the naturally etched surface without preparation in any way.

The iron blade

When the axe first came into the collection the iron blade and the bronze tang were apparently still joined. They eventually became separated and traces of animal glue at the break revealed an old repair. The stump of the blade that still remains in the slot gives convincing evidence that the blade and head belong together.

Although the blade is now a mass of iron rust much scaled and blistered on the surface, it appears to retain quite well its original shape. The fractured edges of both blade and stump show a laminated structure (*fig. 2*). In 1950 the late Dr. William F. Foshag of the Department of Geology, Smithsonian Institution, examined the iron residues and reported, "Sample 34.10 was strongly magnetic containing considerable nickel. This resembles in many respects some oxidized meteoritic iron." (See FGA folder sheet for this object.) This remark about meteoritic iron was the clue that started the long investigation which will be described later in this report.

The inlay

The high relief decor on each side of the axe head and the *t'ao t'ieh* surrounding the central hole was originally inlaid with some sort of material of which only traces remain. Small, reddish brown chunks are visible in the high relief design; one can be seen in *figure 1* (lower), just below and to the left of the left eye of the mask on the haft. The green inlay in the lower design can be clearly seen in the *frontispiece*. When the red chunks in the haft are viewed under a low-power stereomicroscope (at magnifications about ×30) they are seen to have a conchoidal fracture, and the fractured edges are green. X-ray powder diffraction of a number of samples from this area shows some lines which could be attributed to tridymite along with other lines which we cannot identify. All of the patterns are weak and diffuse and show much fluorescence. Powder patterns were also taken from some of the inlay on the lower portion of the weapon, and these are very similar to those from the upper part. All of the inlay material is of similar crystal structure, and it is definitely not turquoise or nephrite.

A sample from the red inlay was removed with a vibrating steel needle, mounted in Canada balsam, and examined microscopically. It consists of fractured particles with brownish inclusions which are so small that they are difficult to resolve with the

optical microscope; they appear to be polygonal grains. The matrix material is isotropic and has a refractive index so close to that of balsam (1.53) that its edges are invisible. The inclusions have a higher refractive index than the matrix and are birefringent. This evidence tends to make one conclude that this material is a glass with crystalline inclusions.

A qualitative spectrographic analysis of the material supports this conclusion. Two samples were taken from the reddish material, and both contained Si, Fe, P, Mg, Al, Ca, and Cu. No Pb was detected. Fe and Cu might easily have come from the close proximity with these materials in the weapon. If it is a glass, it is a lime-silica glass and not a lead glass, a fact which the radiograph confirms.

If one accepts the inlay in this weapon as being glass, and there seems to be no reason to doubt it, the weapon is rendered even more remarkable. Glass beads have been discovered in ninth-eighth century B.C. tombs in China (Chêng, 1963, p. 198), so this object is not a unique use of glass at this period. The inlay in other Shang and Chou weapons should be critically examined to be sure that those labelled "turquoise" are not actually glass.

Radiographic examination

The whole broad axe was X-rayed at the U.S. Naval Ordnance Laboratory near Washington, D.C. The radiograph (see caption, *fig. 5*) reveals various details of structure and condition: (1) There appears to be no large trace of metallic iron in the mass of rust which is all that remains of the exposed part of the iron blade. (2) There is no distinct terminal line for the iron blade, only an indistinct mottled area just inside the slot. (3) There are three nearly evenly-spaced spots of greater density on the edge of the bronze which seem to relate to the device that was used to secure the iron blade to the tang. (4) The bronze tang has been broken across the middle and repaired at the edges with tin-lead solder (see above).

FIG. 5.—34.10. Radiograph of bronze broad axe. The view reveals that the bronze head had previously been broken into three pieces and joined with solder. It also shows three spots of high density along the ferrule edge which were later revealed to be, not rivets, but cast-in cross bars made to secure the iron blade to the bronze head. They indicate also that the bronze head was "cast-on" to the iron. Since the iron blade is almost completely converted to oxide, it hardly shows in the original radiograph, and its appearance has been enhanced photographically here. Radiograph taken at 150 Kv, 10 Ma, distance from target 76 cm.; developed in Eastman Kodak Microdol developer. Courtesy, U.S. Naval Ordnance Laboratory, White Oak, Silver Spring, Maryland.

Construction

A special study was made to determine how the iron and bronze members were locked together. It was previously mentioned that the radiograph reveals three nearly evenly-spaced white spots in the edge of the slot which suggest that rivets of some dense metal were used to secure the iron blade to the head. Probing of the area of one of the spots on the inside of the slot revealed there are two stumps or spurs of bronze which are opposite each other, and moreover they seem to be part of the bronze casting itself. There is no evidence of them on the bronze surface at the edge of the slot. Apparently they are not rivets. The location of the other white spots in the radiograph could not be probed, because of the hardness of the iron rust covering them. The evidence here indicates that the bronze tang was cast on to an iron bit that had already been wrought from iron. It further indicates that prior to the joining, the iron blade was drilled through along the joining edge with three holes. The mold for the bronze tang was then built around the wide end of the bit and the tang was cast on. The molten bronze ran into the holes in the iron and when solidified, the blade and tang were securely locked together (*fig. 6*). The interlock casting of bronze legs and handles to bronze vessels, or vice versa, was well known in China in the latter part of the Chou dynasty and here it seems already to be a developed technique of joining in early Chou (Gettens, 1969, ch. 4).

Repairs

The radiograph showed a break and lead solder repair on both sides of the bronze tang, continuous with the upper line of the cut-out decoration (*fig. 5*). Later the repair join was taken apart and this revealed that the broken edges had been filed, perhaps to make them join better and to permit soldering. Much cuprous oxide along the fracture line also indicates that this is an old break which occurred perhaps at the time of excavation. The metal was too corroded to be effectively joined by tin-lead solder. The pres-

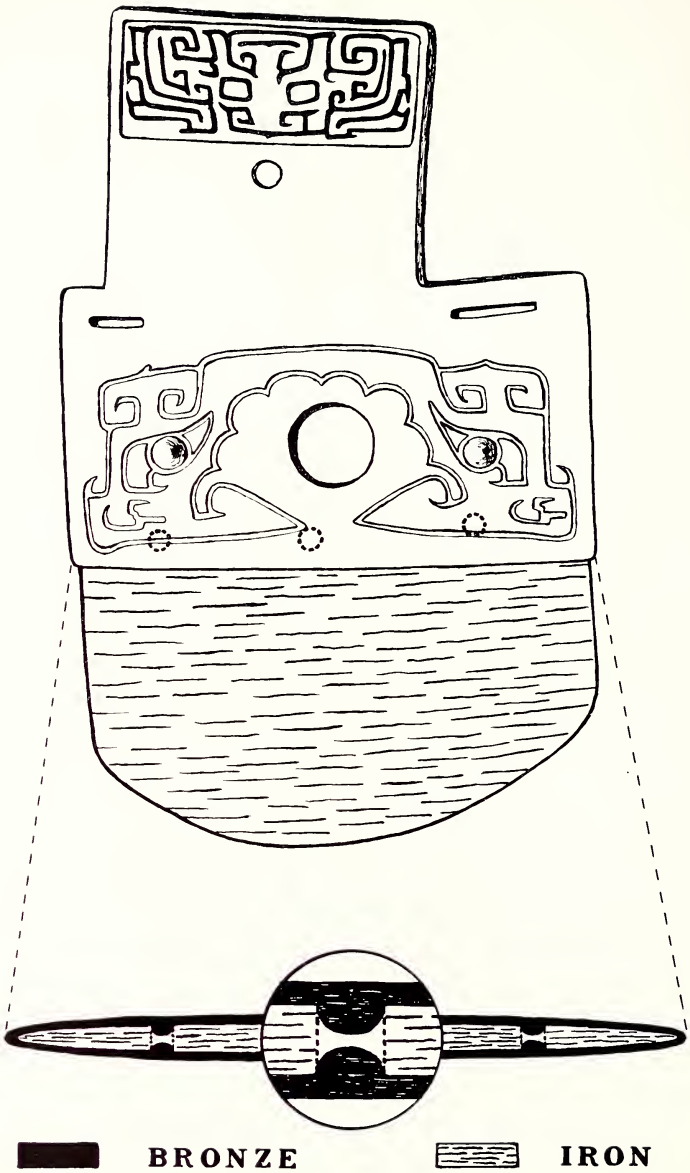

FIG. 6.—34.10. Reconstruction of the ceremonial broad axe with iron blade shows how the bronze tang was cast on and locked to the iron blade.

ence of the repair was outwardly concealed with daubed-on paint in which the modern artificial pigments, Prussian blue and emerald green (Paris green), were identified. The concealment of the repair was aided by scattered splashes of earthy material applied to the surface. These repairs were perhaps made in China before the axe was placed on the antique market.

FIG. 7.—34.11. Two views of a Chinese bronze dagger axe of the type *ko* originally with iron point; dated early Chou dynasty which began in 1027 B.C. It is said to have been dug up with other ancient weapons by a native at Hsün Hsien, Wei-hui-fu, Honan province, not far from An-yang district. Length, 18.3 cm.

III. THE DAGGER AXE (*KO*) 34.11

The object (*fig. 7*), which is 18.3 cm. long and 7.0 cm. wide, weighs 378.5 grams. The blade and tang are cast in bronze, but the point which apparently was originally made of iron, is rusted away and mostly lost. The blade is decorated on either side with a bold dragon motif cast in low relief and the end of the tang is also twice decorated with similar stylized dragon motifs. The tang end of the blade begins in a crosswise hafting ridge, and the inner part, which was covered formerly by a wooden shaft or handle, is flat and undecorated. A plain round hole and a rectangular slot in the heel of the blade probably served to lash the blade to the haft with thongs. The bronze surface is mostly covered with red, blue and green copper corrosion products which are quite decorative. The broken-off end of the blade (*fig. 10*) is encrusted with iron rust, evidence that the blade originally had an iron point.

Chemical composition of the bronze blade

Samples of the bronze were taken by drilling into the edge of the tang with a No. 44 steel twist drill; after drilling, the hole was plugged with threaded copper wire and the spot concealed. Wet analysis for major constituents shows:

Cu	85.5 % (electrolytic)
Sn	12.2 % (gravimetric)
Pb	2.1 % (electrolytic)
Total	99.8 %

The analysis is the average of duplicate determinations made on samples weighing approximately 80 milligrams each (see also Table 5).

Spectrographic analysis on duplicate 10 mg. samples of bronze taken from the core shows in addition to copper, tin and lead the following elements:

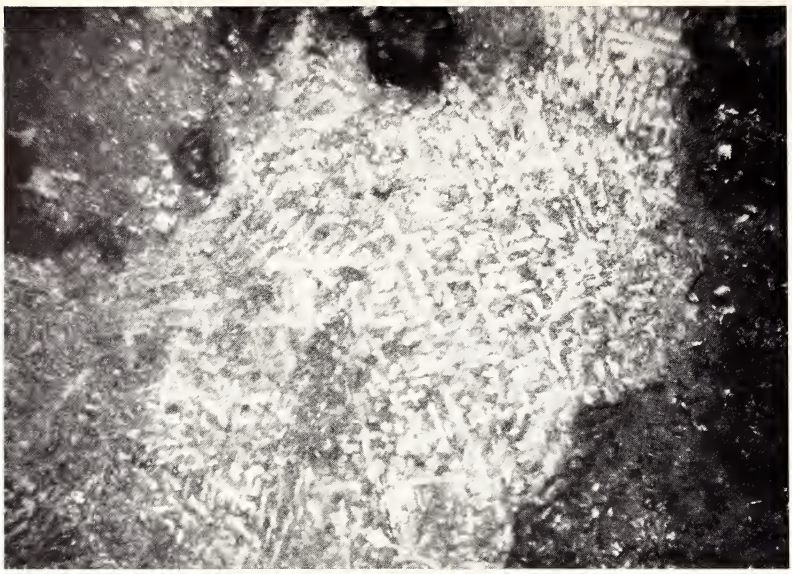

FIG. 8.—34.11. Chinese bronze dagger axe. Several areas of the tang of the dagger still retain the original polished surface of the metal. These smooth surfaces, however, have been naturally etched by the corroding environment sufficiently to reveal the dendritic structure of the cast alloy. Photomicrograph ×75.

FIG. 9.—34.11. Chinese bronze dagger axe. Residues of the wooden handle which was lashed to the bronze axe head still adhere to the copper corrosion products on the surface.

In the range	0.1–1.0 %	Ag, Al, As
In the range	0.01–0.1 %	Co, Fe, Ni, Sb
In the range	0.001–0.01 %	Bi, Si
Less than	<0.001 %	Cr, Mg
Sought but not found		Mn, Zn

The bronze alloy is definitely different from the alloy of the broad axe, but both are made of moderately high tin alpha bronze. Lead content is low which is in contrast to the highly leaded bronze usually found in the ceremonial vessels of this period.

FIG. 10.—34.11. End view (× 2) of Chinese bronze dagger axe, showing the iron rust remains of the original iron point.

FIG. 11.—34.11. Radiograph of the bronze dagger axe. The radiograph shows that the iron rust deposit at the point end conceals an open dragon's mouth and that the bronze blade was cast-on to the point which had been shaped in the form of a key so that bronze and iron are securely locked together. Radiograph taken at 250 Kv, 10 Ma, distance from target 183 cm.; developed in Eastman Kodak Microdol developer. Courtesy, U.S. Naval Ordnance Laboratory.

Metallographic structure

A small unencrusted area on the tang indicates that the metal was originally well polished to an almost mirror-like surface but ghosts of dendritic structure show in the little-corroded areas of the surface (*fig. 8*) which further indicates the bronze was cast.

Corrosion products

The bronze surface is covered in certain areas with patches of blue azurite and green malachite. A fairly solid layer of cuprite underlies the basic copper salts. No atacamite (basic copper chloride, $Cu_2(OH)_3Cl$) was found. The high total percentage of Cu, Sn and Pb in the chemical analysis indicates that corrosion has not penetrated deeply into the metal core. Neither tin nor lead corrosion products show on the surface. The undecorated area on one side of the tang is traversed with parallel striations crosswise on the blade which were recognized as impressions or residues of the original wooden haft (*fig. 9*). There were not sufficient diagnostic features left in the wood cell structure to identify the species or even the genus of the wood.

The iron point

As previously stated no actual point exists; only the rusty residues of what is presumed to have been a point at the end of the bronze blade. Dr. W. F. Foshag examined, in 1950, samples of these rusty accretions at the same time he examined the rusty blade of the broad axe and found that, "Sample 34.11 was not magnetic, contained some copper; but no nickel was detected. This specimen of oxidized iron is not believed to be from a meteorite." (See FGA folder sheet for this object.) The specific studies on the iron residues, which will be reported later, indicate strongly, however, that the original iron of this weapon was also meteoritic in origin and they explain why Dr. Foshag failed to reach that conclusion.

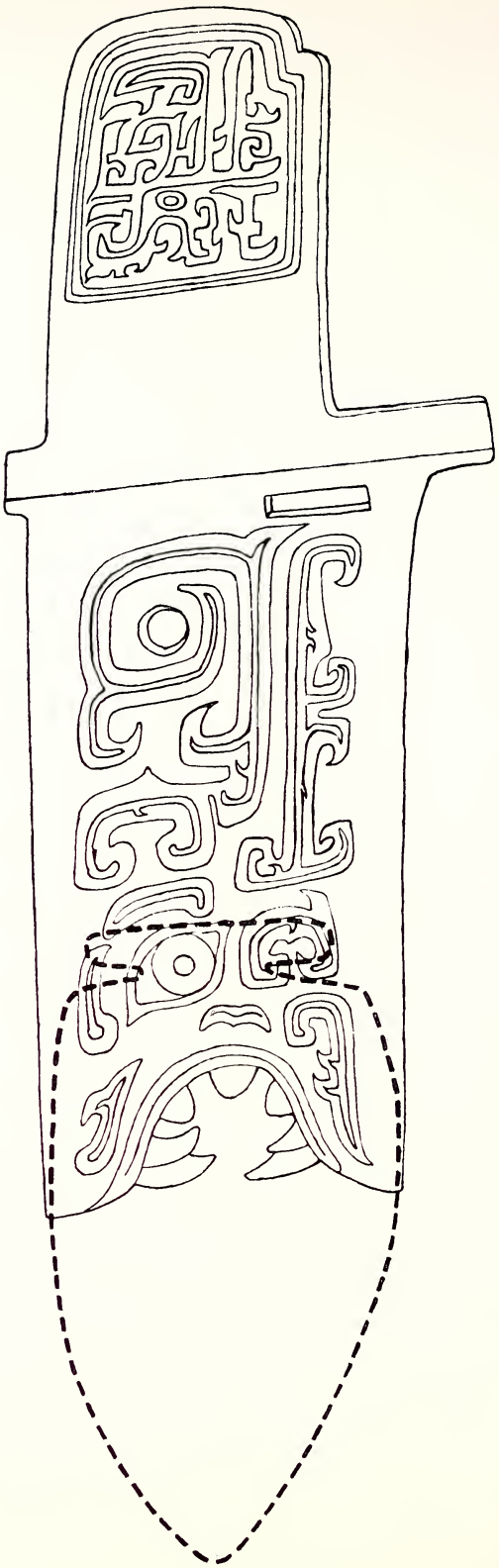

FIG. 12.—34.11. A reconstruction of the Chinese bronze dagger axe, shows how the iron point looked originally and how the bronze blade was cast-on and locked to the iron.

Radiographic evidence of the method of construction

This axe was also X-rayed at the U.S. Naval Ordnance Laboratory and the radiograph revealed some striking features of construction (*fig. 11*). It shows that the bronze blade terminates in the gaping mouth of a dragon which grasps the iron point in its teeth. Less dense areas just back of this open mouth show that the butt of the iron point terminated in a double notched tang or key by which it was secured to the blade. Small drill holes made in this area confirmed the presence of a layer of iron oxide sandwiched between the two outer layers of bronze. It is probable that the mold for the bronze blade was built around the keyed end of the iron point so that when molten bronze flowed in and around the key and solidified, the blade and point were securely locked together. Again we have an example of lock-on casting. In the reconstruction of the axe (*fig. 12*) it appears that the dragon is swallowing the iron point.

The bronze blade is cast in one piece probably in a bivalve mold. The only signs of mold marks are on the square ends of the hafting ridge. There are no mold marks on the inside of the thong holes.

Original appearance

It is difficult to say just how the dagger-axe looked originally, but the iron point was probably about 7–8 cm. long, making the total length of the weapon about 23–25 cm. (*fig. 12*). There are in existence many all-bronze dagger axes of this same style and period. From pictures on tomb tiles of the Han period, and from other sources we can imagine that the handle of the axe was a simple staff with a slot cut in near the end to accommodate the tang and that the dagger axe was secured to the staff by thongs laced through the slot and hole. Max Loehr (1956, ch. III) shows illustrations of Shang pictographs which give some idea of the way dagger axes were hafted.

FIG. 13.—34.11. Chinese bronze dagger axe. The macrograph (× 10) shows traces of a laminated structure in the iron rust which is characteristic of the mineral goethite. This small area of laminated structure occurs about 2 cm. from the end of the bronze blade in an area of rust that was transported and deposited on the bronze surface.

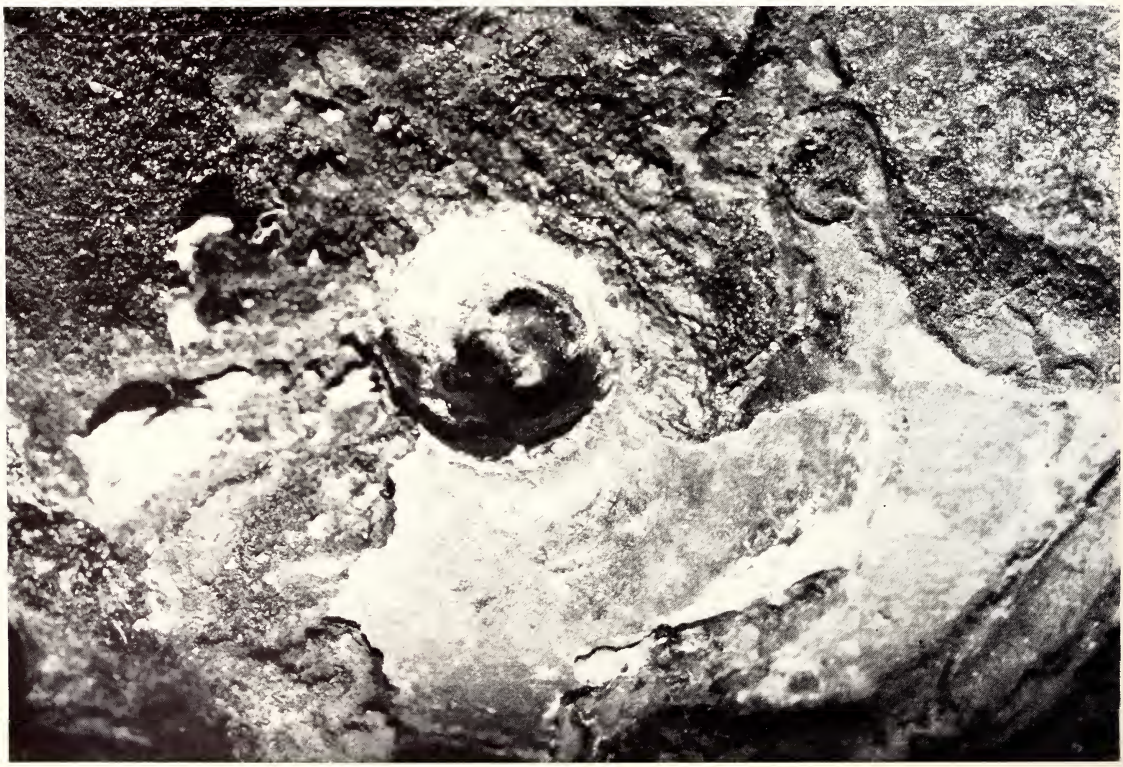

FIG. 14.—34.11. Chinese bronze dagger axe. The macrograph (× 9.2) shows a drill hole that was made near the end of the bronze blade passing through the outer encrustation of iron rust, through the bronze layer and into the inner iron core. After about five years in storage, a crusty brownish globular shaped deposit of ferric chloride formed in the drill hole.

IV. STUDIES ON THE OXIDE RESIDUES OF THE IRON BLADE AND IRON POINT

Early in the study it became evident that the iron residues are of special interest, not only because the weapons date from a period which precedes the accepted date for the beginning of the iron age in China, but also because Dr. Foshag made the inference in his early findings that the iron of the broad axe contains enough nickel to suggest that it might be of meteoritic origin. This interest initiated studies which, over a period of some years, have confirmed the meteoritic origin of the iron of the broad axe and have also indicated that the iron of the dagger axe probably had a similar origin.

Remnant oxides of the blade of the broad axe 34.10

The iron blade which served as the cutting edge has been drastically altered by corrosion. The radiograph which reveals many details of the bronze tang is very dark opposite the area of the blade indicating almost complete absence of metallic iron. X-ray powder diffraction analysis of samples of rust showed that it consists of two hydrated iron oxides, goethite, alpha FeO(OH) and lepidocrocite, gamma FeO(OH), dimorphous with goethite, and three anhydrous oxides, magnetite, Fe_3O_4, maghemite, gamma Fe_2O_3, and hematite, alpha Fe_2O_3. The rusty mass is sufficiently magnetic to permit the blade to be raised free from the table with a strong magnet.

Remnant oxides of the point of the dagger axe 34.11

The rust residues cover the blunt end of the bronze blade in an irregular crusty mass. X-ray diffraction analysis of the outer exposed crusts shows presence of only the hydrated oxides goethite and lepidocrocite. (This is apparently where Dr. Foshag got his sample.) One small area (*fig. 13*) has ripple marks which are characteristic of naturally formed goethite. There is a cleft in the

end of the blade which divides the iron rust in two parts (*fig. 10*). There is no obvious reason for this but it may demonstrate the completeness of the transfer of iron salts from their initial position, or it may simply be geometric distortion caused by the oxidation of the iron with expansion of volume. The rust-covered end of the blade rises to a strong magnet. Since goethite is not magnetic it was suspected that the remnant oxides in the interior in the neighborhood of the key revealed by the radiograph might be magnetite. To test this idea small exploratory borings were made into the interior, which confirmed the presence of iron oxide; and furthermore, X-ray diffraction analysis showed that the iron oxide deep in its interior is magnetite, not goethite. This explains the attraction to the magnet of the end of the bronze blade. Apparently the conditions in the interior of the blade favored formation of magnetite over goethite.

The exploratory drill holes were made in 1956 before the installation of air-conditioning in the gallery. After about five years in storage it was observed that a bubble-like reddish brown crust had formed in the drill holes (*fig. 14*). The crust was glossy and amorphous, like a solidified gel; it dissolved in dilute nitric acid and tested strongly for chloride ion. Apparently unstable iron chlorides are present and since these are strongly hygroscopic they may account for the transport of iron compounds from the iron point to the bronze surface. The presence of iron chloride may also explain the rapid disappearance of most of the original iron point. It is strange, however, that no evidence of chloride salts were observed among the copper corrosion products.

Sampling

At this point it was decided that more precise information was needed about the composition of the iron oxides of both weapons. Small chips were removed from the broken-off end of the iron blade and borings were made into the split end of the dagger axe in an attempt to get oxide from deeper in the interior where it should be less altered. These samples were ground to a fine powder

in an agate mortar and subsamples were taken for X-ray diffraction analysis (see above) and spectrographic and chemical analysis. The total amounts of sample prepared for analysis were 580 mg. for the broad axe (34.10) and 740 mg. for the dagger axe (34.11). (It will be more convenient from now on to report laboratory findings on the iron oxides of both weapons together than to keep them separate as has been done previously.)

A subsample of each oxide sample was examined for strongly magnetic material using a hand magnet. The broad axe blade (34.10) sample yielded 72 percent by weight of magnetic material and a non-magnetic fraction. X-ray diffraction analysis indicated that the magnetic material was largely magnetite with small amounts of maghemite, goethite and hematite. Only goethite and lepidocrocite were indicated for the nonmagnetic fraction. Magnetic separation of the dagger axe sample indicated less than one percent magnetic material, too little to examine further.

Semiquantitative spectrographic analysis

Approximately 30 mg. portions of both oxide samples were submitted to the U.S. Geological Survey for semiquantitative spectrographic analysis. The elements that were detected and their approximate concentration ranges are listed in Table 1. The spectrographic procedure used has been described by Waring and Annell (1953), and their paper lists detectability data for individual elements.

Chemical analysis

The oxide samples described above were quantitatively analysed for their major constituents and the results are given in Table 2. Water was determined by the Penfield method without flux on separate 158 mg. (broad axe, 34.10) and 150 mg. (dagger axe, 34.11) samples. The other constituents were all determined on single samples of 228 mg. (34.10) and 205 mg. (34.11).

The oxide samples were dissolved in dilute HCl for major constituent analysis. A closed system swept with nitrogen was used

TABLE I

Semiquantitative spectrographic analyses
of iron oxide samples*

Element	I Broad axe (34.10) † percent	II Dagger axe (34.11) † percent
Si	0.7	0.5
Al	0	.001
Fe	M	M
Mg	.005	.03
Ca	.015	.03
Ti	.0015	.005
Mn	.0003	.0005
Ag	0	.00007
Ba	.05	.0015
Be	.00007	.0007
Co	.15	.05
Cr	.0005	.0007
Cu	0.3	0.5
Ge	.005	.005
Ni	3.0	0.5
Pb	.007	.003
Sn	.01	0.15
Sr	.0007	0

* Analyst: Nola Sheffey, U. S. Geological Survey.

† Results are reported in percent to the nearest number in the series 1, 0.7, 0.5, 0.3, 0.2, 0.15 and 0.1, etc: which represent approximate midpoints of group data on a geometric scale. The assigned group for semiquantitative results will include the quantitative value about 30% of the time.

M = major constituent — greater than 10%
O = looked for but not detected

Note. The following elements were looked for but not detected in either sample: Na, K, P, As, Au, B, Bi, Cd, Ce, Ga, Hf, Hg, In, La, Li, Mo, Nb, Pd, Pt, Re, Sb, Se, Ta, Te, Th, Tl, U, V, W, Y, Yb, Zn, Zr.

and the evolved gas passed through a solution of lead acetate. No precipitate formed, indicating the absence of significant quantities of acid-soluble sulfide. The insoluble residue from the sample solution was a colorless material which was filtered, ignited and weighed. On ignition the residue from the broad axe (34.10) oxide developed a slight brown color, while the residue from the dagger axe (34.11) oxide became rose colored. X-ray powder analysis of these residues indicated that alpha quartz was the major constituent. The sample solution was evaporated to dryness in glass after the addition of 5 ml. of HNO_3. Acid soluble SiO_2 was dehydrated by this treatment, collected on paper, ignited, weighed, and the loss in weight determined after HF volatilization. The HCl solution from the separation of SiO_2 was taken to 100 ml. in a volumetric flask, and this solution was used as a working solution for the determination of other constituents. Ni was determined on a 50 ml. aliquot using a standard gravimetric method, precipitation with dimethylglyoxime from a tartaric acid solution. Total iron was determined on a 20 ml. aliquot by titration with standard $K_2Cr_2O_7$ after reduction by a silver reductor. Co was determined on a 5 ml. aliquot using the nitroso-R method as described by Moss, Hey and Bothwell (1961).

Three additional small samples from the dagger axe (34.11) oxide were partially analysed by the same general procedures in an unsuccessful attempt to find material of higher Ni content. These results are also reported in Table 2. Approximate sample weights used were III, 185 mg; IV, 240 mg; and V, 130 mg. A 50 ml. aliquot of 100 ml. of solution was used for the Ni determination. Sample IV was also separated with a magnet, and a 2 percent strongly magnetic fraction was recovered, confirming a similar measurement mentioned above. X-ray diffraction analysis of this fraction indicated magnetite and maghemite with small quantities of goethite and hematite. The nonmagnetic fraction, the bulk of the sample, contained mainly goethite with some lepidocrocite and a little hematite.

Analysis I in Table 2 is presented in two ways. In (a) all of the Fe is calculated as Fe_2O_3. This leads to a high total and con-

TABLE 2

Chemical analyses of oxide samples*

	I Broad axe (34.10) (a)	(b)	II Dagger axe (34.11)	III Dagger axe (34.11)†	IV Dagger axe (34.11)‡	V Dagger axe (34.11)§
Ignited insoluble residue	2.6%	2.6%	1.2%	0.5%	0.3%	0.3%
Acid soluble SiO_2	0.1	0.1	1.1			
Fe_2O_3	74.1		82.3			
NiO	8.53		0.80	1.1	1.3	0.74
(Ni, Fe) Fe_2O_4		80.8				
CoO	0.16	0.16	0.05			
Total H_2O	16.0	16.0	13.6			
Totals	101.49	99.66	99.1			
Cu(spectrographic)	0.3	0.3	0.5			

* Analyst: Roy S. Clarke, Jr.
† Chips from edge of fissure.
‡ Drillings inside fissure.
§ Deeper drillings inside fissure.

TABLE 3

Analyses of magnetic and nonmagnetic fractions of broad axe (34.10) blade oxide*

	Nonmagnetic portion 59 mg.	Magnetic portion 151 mg.	Composite	I (a) (from Table 2)
Ignited insoluble residue	4.2%	2.0%	2.6%	2.6%
Fe_2O_3	66	76	74	74.1
NiO	8.0	8.6	8.5	8.53
CoO	.26	.20	.21	.16
Loss on ignition	19	13	15	
Total H_2O				16.0

* Analyst: Roy S. Clarke, Jr.

flicts with the X-ray data which indicates that most of the Fe is present as magnetite. In (b) all of the Fe and Ni are accounted for in the magnetite formula, (Ni, Fe) Fe_2O_4, and a more satisfactory total results. Calculation (b) is undoubtedly nearer to the correct presentation than (a). The true value, however, must be between these extremes.

The magnetic (151.3 mg.) and nonmagnetic (59.4 mg.) fractions of sample I (broad axe, 34.10) were also analyzed by the same general procedures used above. The results of this partial analysis are given in Table 3. Because of the small samples available loss on ignition was determined instead of total H_2O, simply by moderate heating over a Meker burner for approximately 15 minutes. This determination gave information similar to the H_2O dermination made previously and permitted the same sample to be used for all of the determinations reported. The residue from the ignition was dissolved with prolonged digestion in mixed HCl-HNO_3 and finally evaporated to dryness. The residue was taken up in dilute HCl, the insoluble material filtered off, and the filtrate made to 100 ml. Aliquots were taken for Ni (50.0 ml.) and Fe (20.0 ml.), and the procedures outlined above were employed. The accuracy of these results is lower than in the previous analyses due to small sample size. This is indicated in the table by the use of fewer significant figures in the reported values. It is interesting, however, that the calculated composite analysis based on these figures agrees well with corresponding figures obtained directly on sample I.

Oxide composition

The chemical and X-ray data presented thus far serve to characterize the bulk properties of the remnant iron oxides associated with these bronze objects. The optical and electron microprobe work that will be discussed later was done on similar samples of oxide. While this work is concerned mainly with the identification of metallic inclusions within the oxide matrix, additional data on a micro scale will be given on oxide composition and

characteristics. These data are consistent with the conclusions that are drawn in this section.

The X-ray diffraction data already mentioned indicate that the two remnant materials are mixtures of several oxides of iron. These are goethite, lepidocrocite, magnetite, hematite, and maghemite. The chemical and spectrographic data support this view. The spectrographic data also show that from a relatively large group of elements none is present in quantities that would be inconsistent with oxide derived from the weathering of meteoritic material. The small amounts of the elements Si, Ca, Ba, Cu and Sn that were found (Table 1) can be explained on the basis either of condition of burial or the fact that the blade had been fabricated to a bronze object. The important fact is that the major elements present were Fe, Ni and Co, the major elements of iron meteorites.

The data above indicate that the two oxide materials have much in common compositionally. Their important difference is that sample I, the broad axe blade oxide, is largely magnetite and contains appreciably more Ni and Co than the dagger axe oxide. It is reasonable to expect that weathering which produces magnetite from a Ni-containing material would retain more Ni than weathering that produces goethite and lepidocrocite. Magnetite has a 2-valent cation crystallographic site, normally occupied by ferrous iron, which is a favorable host position for Ni. Nickel-ferrous iron substitutions are well known in mineralogy, the two ions having the same plus 2 charge and similar ionic radii. Iron oxides with only 3-valent cation positions such as goethite and lepidocrocite are known as poor hosts for Ni. Buddhue (1957) has summarized data from the meteorite literature along with observations of his own that support this point. Iron oxides resulting from the weathering of iron meteorites vary greatly in the amount of Ni they contain. In some cases the oxide residue has lost essentially all of the Ni from the parent meteorite.

The data in Table 3 show that three quarters of the total Ni present in sample I is associated with the magnetic fraction. This material has been shown by X-ray diffraction to be essentially

magnetite. The analyses of the dagger axe (34.11) oxide (Table 2, analyses II, III, IV and V), which is essentially a mixture of goethite and lepidocrocite, show that much less Ni has been retained by these hydrous oxides. A reasonable explanation of the observed mineralogy and consequent differing Ni contents in the remnant oxides would be slightly different conditions of oxide development during burial. The controlling factors in such a case might be the effective oxidation potential and acidity. It is, of course, not reasonable to assume constant conditions throughout the period of oxide development, but this approach may give a simplified view of what took place. Magnetite is stable under mildly reducing conditions in solutions that are slightly alkaline. More oxidizing conditions result in hematite formation over a broad range of conditions from mildly acid to strongly alkaline (Garrels and Christ, 1965). At a given acidity, a minor change in oxidizing conditions could mean the difference between magnetite or hematite formation. The specific conditions that lead to magnetite formation are also favorable for Ni retention. Oxidation potentials in a burial site would be affected by soil and ground water acidity, water table levels, the presence of reducing materials such as decaying organic matter, and possibly other factors. Significantly different oxidation potentials can be operative over distances separated by a few centimeters, or even less. A fairly broad range of oxidation conditions could exist within a single burial.

Sampling for optical and electron microprobe examination

Chips of the remnant oxide were removed from the two weapons for optical and electron microprobe examination. The samples were mounted in plastic and highly polished surfaces were prepared by standard methods. One mount contained 10 fragments of the broad axe (34.10) blade oxide. Three of these fragment surfaces are shown in *figure 15*. Two mounts were prepared from dagger axe (34.11) oxide fragments. The single fragment in one of these mounts is shown in *figure 16*. *Figure 17* is a macro-

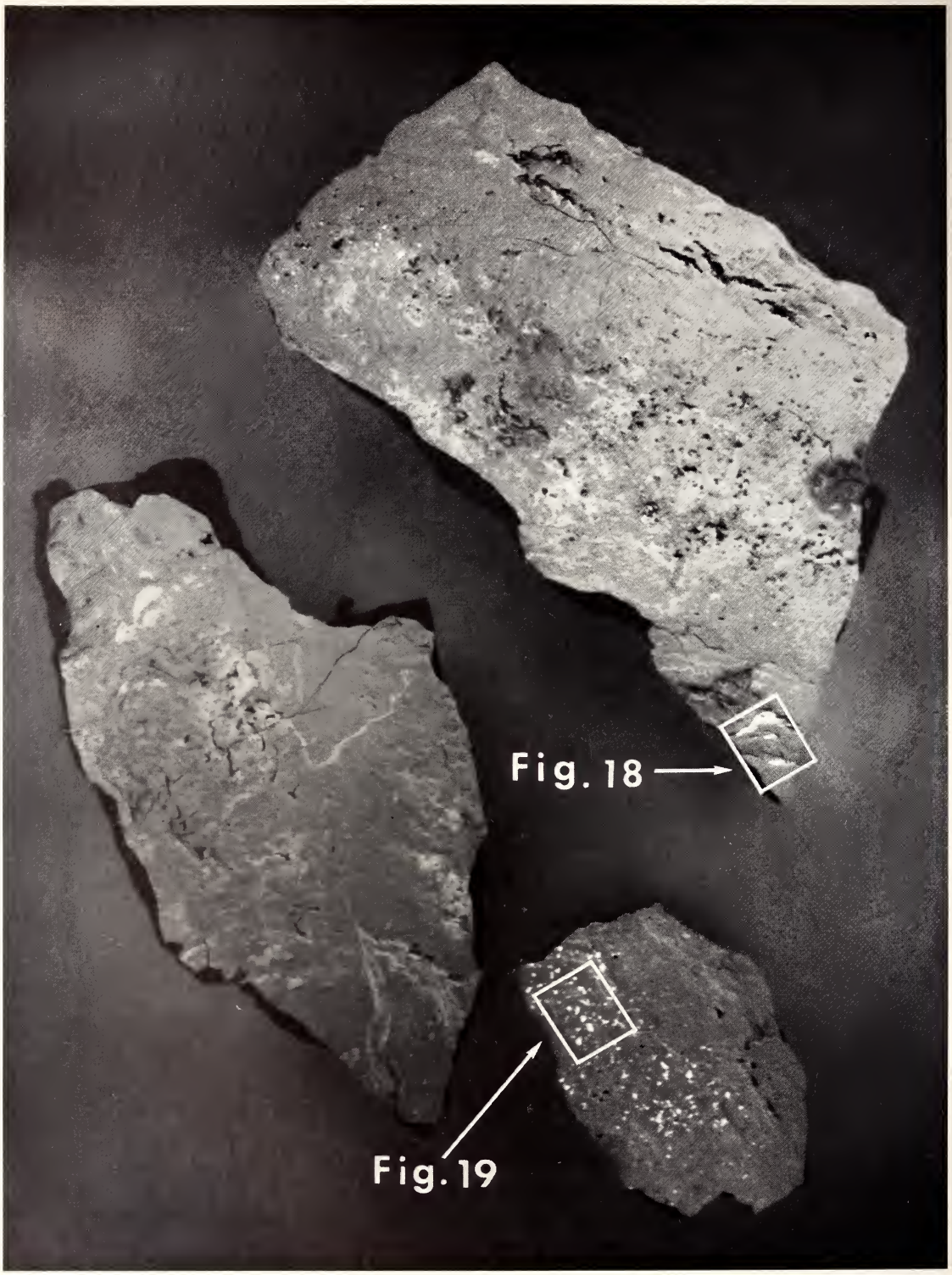

FIG. 15.—34.10. Fragments of remnant oxide from metal blade of the broad axe, mounted in plastic and polished for microscopic and electron microprobe examination; ×20. Small bright areas are remnant metal. Marked areas indicate location of photomicrographs (see *figs. 18* and *19*).

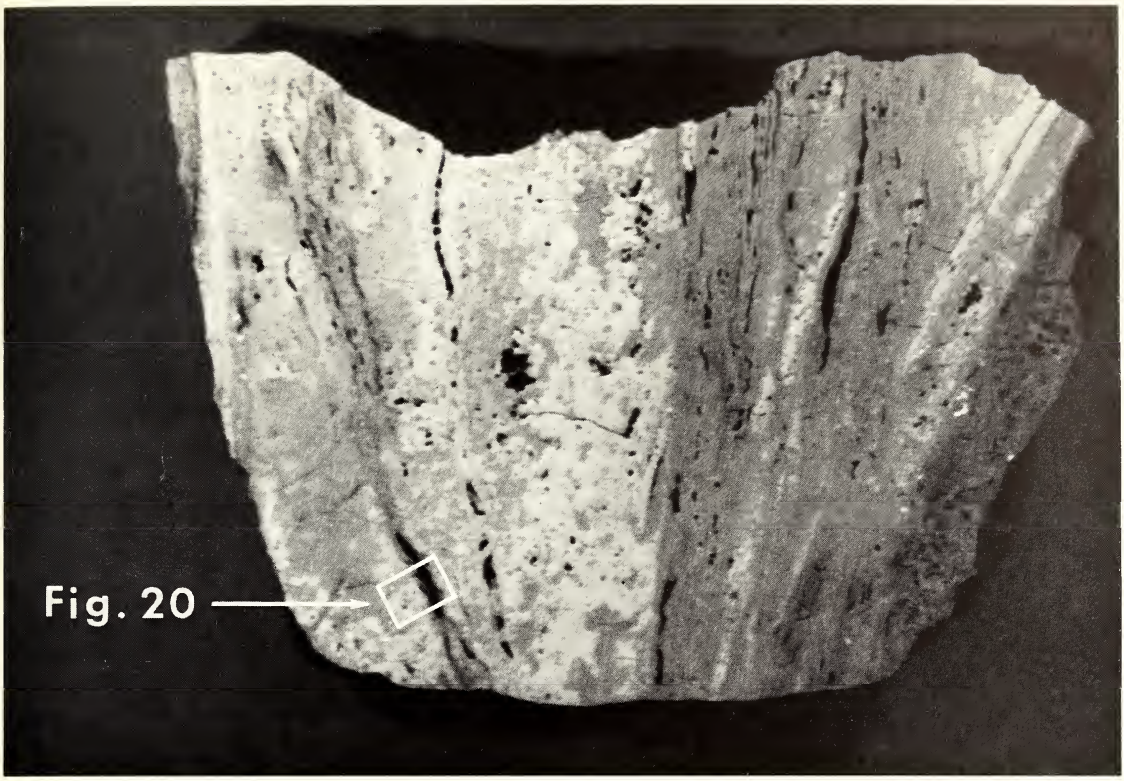

FIG. 16.—34.11. Fragment of remnant oxide from metal blade of the dagger axe, mounted in plastic and polished for microscopic and electron microprobe examination; approximately ×25. Marked area shows location of *figure 20*.

graph of the surface of the second mount of dagger axe (34.11) material containing five fragments. The mounts were prepared in the laboratory of the Mineralogical Institute, University of Heidelberg, Heidelberg, Germany, preliminary to optical examination by Professor Paul Ramdohr.

Professor Ramdohr's completely independent examination of these oxides using the techniques of reflected light microscopy provided an important stimulus to more detailed work. It was undertaken at a comparatively early stage in our investigations. The chemical and X-ray studies described above were nearing completion, and it had become obvious that this work alone would not permit a strong case to be built for a specific origin for the material from which these oxides were derived. More specific data were needed.

FIG. 17.—34.11. Fragments of remnant oxide from metal blade of dagger axe, mounted in plastic and polished for microscopic and electron microprobe examination; ×15. The lines indicate the path of electron microprobe traces.

In an oral report to one of us (Roy S. Clarke, Jr., March 25, 1964), Professor Ramdohr summarized his findings based on the examination of the polished mounts. He found ample evidence to conclude that the broad axe (34.10) blade oxide was very probably derived from a meteorite. He observed about 2 percent metal in this section, including the three meteoritic minerals kamacite, taenite, and some troilite. Kamacite is an alloy of Ni-Fe containing 4.5 to 7.5 % Ni, while taenite is an alloy of Ni-Fe contaning more than 20 % Ni. Kamacite has a body-centered cubic structure and is also known as alpha-iron or ferrite; taenite has a face-centered cubic structure and is also known as gamma-iron or austenite. Troilite is a meteoritic sulfide (stoichiometric FeS). The bulk of the sample was reported to be magnetite and maghemite with a little limonite (goethite). The magnetite had the patchy appearance of high Ni magnetite, typical of a weathered meteorite. Ramdohr observed remnant meteorite structures and suggested that the presence of taenite lamellae was particularly significant. He also concluded from microscopic evidence that the taenite lamellae had been hot-worked prior to the onset of weathering of the blade.

Ramdohr's examination of the dagger axe (34.11) oxide did not convince him that it was derived from a meteorite. He reported that it was largely limonite with inclusions of Cu.

Work to be discussed below has confirmed the validity of Ramdohr's identifications and the major conclusion drawn about the broad axe (34.10) blade oxide. Additional data obtained by microprobe analysis has confirmed the mineral identifications in the dagger axe (34.11) point oxide, and allowed us to conclude that this oxide, too, may well be meteoritic in origin.

Electron microprobe studies

Studies employing an electron microprobe have extended and confirmed the chemical and optical investigations described above. An electron microprobe is an intricate modern instrument used to obtain chemical analyses from small volumes of the surface of a solid sample by analysis of emitted X-rays. The possibility of this

type of analysis was implicit in Moseley's (1913) early work on X-ray spectra. Castaing (1952) was the first to construct an analytical instrument, and he made fundamental contributions to the development of the basic theory and philosophy of quantitative application. In brief, the instrument focuses a narrow beam of electrons on a polished sample surface in vacuum, the beam size frequently being as small as one micron (0.001 mm.) in diameter. Characteristic X-rays are emitted from a small volume of sample, the spectra emitted depending on the composition of the sample and the energy of the impinging electrons. The wavelengths of the emitted X-rays are determined by curved-crystal spectrometers, and the intensities of the X-rays are measured by appropriate counting devices. X-ray wavelengths identify the elements present, and specific intensities relate to the amount of a given element present. Recent reviews describing quantitative electron-probe analysis in detail have been given by Birks (1963) and Keil (1967). Archaeological researchers have made good use of the electron microprobe in studying specific problems; see, for example, the work of Hornblower (1963), Young (1963), Brill and Moll (1963) and Lechtman (in press).

The analytical data reported here were obtained in the laboratory of the Division of Meteorites of the National Museum of Natural History, Smithsonian Institution, using a modified electron microprobe built by the Applied Research Laboratories, Glendale, California.

Photomicrographs of the areas of the polished sections that were analyzed by the microprobe are shown in *figures 18–20*. The locations of these areas are indicated on *figures 15* and *16*. The photomicrographs were taken on a Vickers Projection Microscope, an instrument designed primarily for metallographic application.

Figure 18 is of an area of broad axe (34.10) blade oxide containing lamellae of bright metal that appear to be corroded and distorted taenite. Taenite is a meteoritic mineral containing Fe, fairly large amounts of Ni, and some Co (see above). The matrix is a mixture of oxides of varying composition and patchy appear-

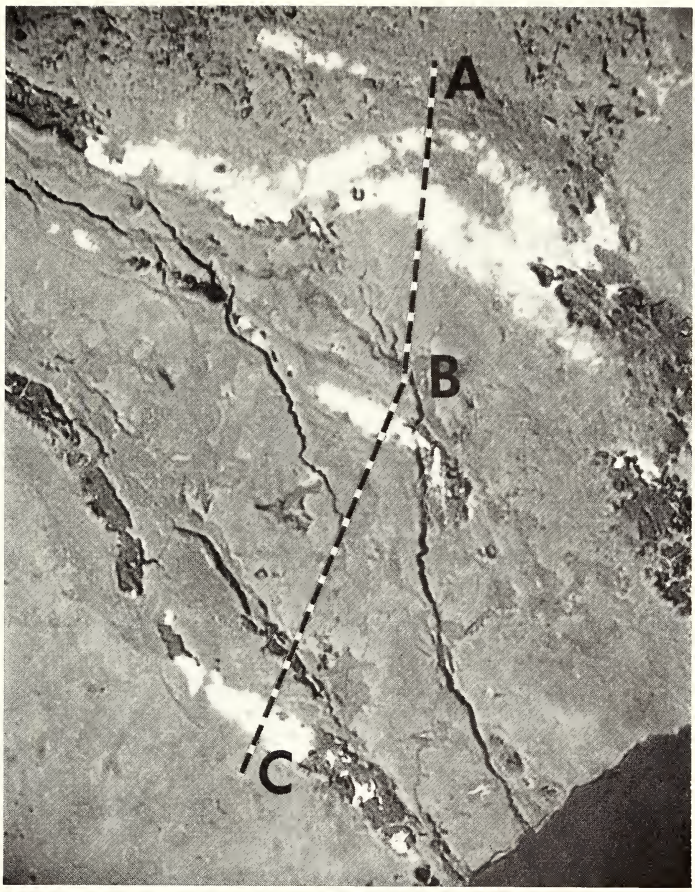

FIG. 18.—34.10. Photomicrograph (× 230) of a metal-containing area of the broad axe oxide (detail of *fig. 15*). The bright metal is taenite and the general structure is suggestive of Widmanstätten pattern. The line indicates the path of the electron microprobe trace in *figure 21*.

ance. Cracks and a few small holes are also present. *Figure 19* is an area from a different oxide fragment of this same object. This area contains many small blebs of bright metal that appear to be corroded kamacite. Similar appearing material is also present in the oxide fragment containing the suspected taenite. Kamacite is also a meteoritic mineral containing Fe, Ni and Co. The Ni content of kamacite is smaller than that of taenite, the maximum Ni content being about 7.5 percent. Co content of kamacite tends to be higher than in taenite.

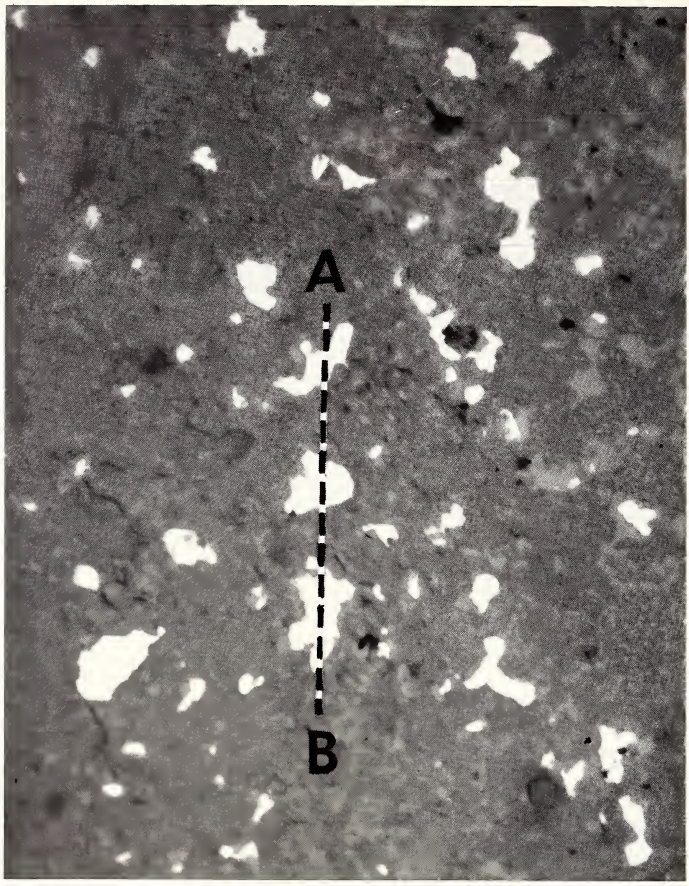

Fig. 19.—34.10. Photomicrograph (×230) of metal containing area of broad axe oxide (detail of *fig. 15*). The bright metal is kamacite. The line indicates the path of the electron microprobe trace in *figure 22*.

Figure 20 is an area in the oxide from the dagger axe (34.11) blade; it is one of the few areas in the six mounted fragments of this oxide that contains remnant metal of possible meteoritic composition. Metal in other parts of this material was found to contain major amounts of Cu and was therefore considered to be related to the bronze alloy in the immediate environment. The area of the photomicrograph contains a number of very small, bright areas that were unidentifiable under the microscope. They are possibly badly oxidized remnants of kamacite or taenite. This

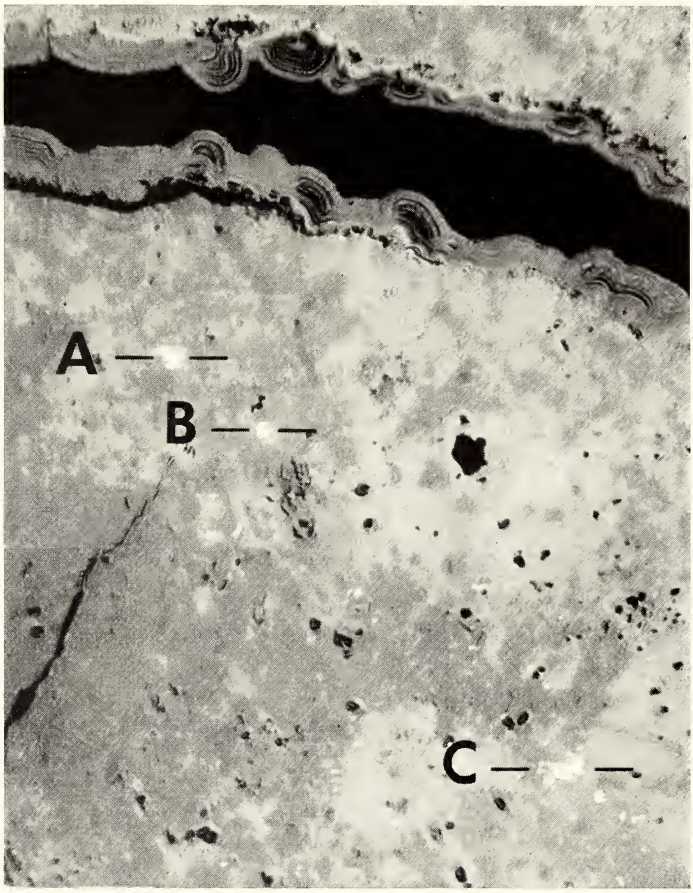

FIG. 20.—34.11. Photomicrograph (×230) of dagger axe oxide (detail of *fig. 16*). The small bright metal areas are not completely resolvable but seem to be of kamacite composition. The letters indicate locations of electron microprobe traces in *figure 23*.

area also contains patchy oxide, a number of small holes, and one large crack. The botryoidal development of the oxide along this large crack is a typical habit of this material.

Several spots from each of the areas shown in the photomicrographs (*figs. 18–20*) were selected for quantitative microprobe analysis. The results are given in Table 4. Analyses 1 and 2 are from the approximate area of *figure 19*, while analyses 4 through 7 are from the area of *figure 18*. Analysis 3 is from the lighter area shown at the left corner of the upper particle in *figure 15*. Analyses

8 and 9 are from the area of *figure 20*. They were performed using two spectrometers simultaneously. Fe and Ni were determined, followed by Fe and Co from the same spots. Both optical observation and total Fe counts were used to establish that all three elements were determined on the same spots. The following standards were used: 100% Fe, 100% Ni, 100% Co, 5% Ni–95% Fe, and 50% Ni–50% Fe. Conventional background, absorption and fluorescence corrections were made. Several of these same specimen areas were also checked qualitatively for the presence of other elements by scanning the emitted X-ray spectrum. Elements present in significant amounts with atomic numbers greater than 11 (Na) would be detected by this procedure. Fe, Ni, Co and traces of P were the only elements found. A particularly careful check was made for the presence of Mn in the metal areas, but it was not detected. The only element observed which had not been noticed previously is P. It was not sought by wet chemical procedures, and the spectrographic procedures used are relatively intensitive to P. On the other hand the electron microprobe is relatively sensitive to P, and this element is generally present in the range of 0.1 to 0.3 percent in iron meteorites. These findings are consistent with the chemistry of meteorite corrosion as discussed above.

The individual analyses in Table 4 strongly suggest that material of both kamacite and taenite compositions are present in the broad axe (34.10) blade oxide. Analyses 1 through 3 are typical of meteoritic kamacite. Analyses 4 through 7 suggest taenite, but the totals are somewhat low. The absence of other elements of atomic number greater than Na and the physical condition of the material being analyzed make this a readily explainable result. The metal areas are small and undoubtedly thin. The X-ray producing volume of sample undoubtedly contains oxide, but oxygen is not detectable by this technique, leading to a low summation. The same explanation undoubtedly applies to the metal-containing area analyses of the dagger axe (34.11) oxide. These areas are so small that oxide must be included in the probe analysis sample. The important observation is that the metal undoubtedly

TABLE 4

Electron microprobe analyses of metallic inclusions in broad axe (34.10) and dagger axe (34.11) oxides*

Sample	Analysis No.	Ni %	Fe %	Co %	Total %
34.10	1	6.9	92.2	.6	99.7
	2	6.7	92.6	.7	100.0
	3	6.8	91.6	.6	99.0
	4	23.0	65.3	.3	88.6
	5	22.6	70.0	.3	92.9
	6	27.3	62.4	.3	90.0
	7	29.3	65.4	.2	94.9
34.11	8	5.2	86.0	.4	91.6
	9	5.2	81.5	.3	87.0

* Analyst: Joseph Nelen.

contains only Fe, Ni and Co in greater than trace amounts, and that the ratios of these elements are appropriate to meteoritic kamacite.

A careful examination of other areas of dagger axe (34.11) oxide was undertaken with the microprobe. Traces for Fe and Ni were made across four fragments as indicated in *figure 17*. The sample was moved under the electron beam at a rate of 96 microns per minute, and a distance of approximately 6400 microns was traversed. Ni varied from approximately 0.5 percent to a maximum of about 4 percent, with Fe varying little from 55 percent. Ni values generally were in the 1 to 2 percent range, and only infrequently above 2 percent. No additional areas were found that seem to contain either remnant taenite or kamacite.

Simultaneous electron microprobe traces for Ni and Fe were also made in three metal-containing areas where quantitative probe analysis had been done (see Table 4). Samples were moved under the electron beam at a rate of 8 microns per minute. *Figure 21* is a reproduction of the trace across the oxide (broad

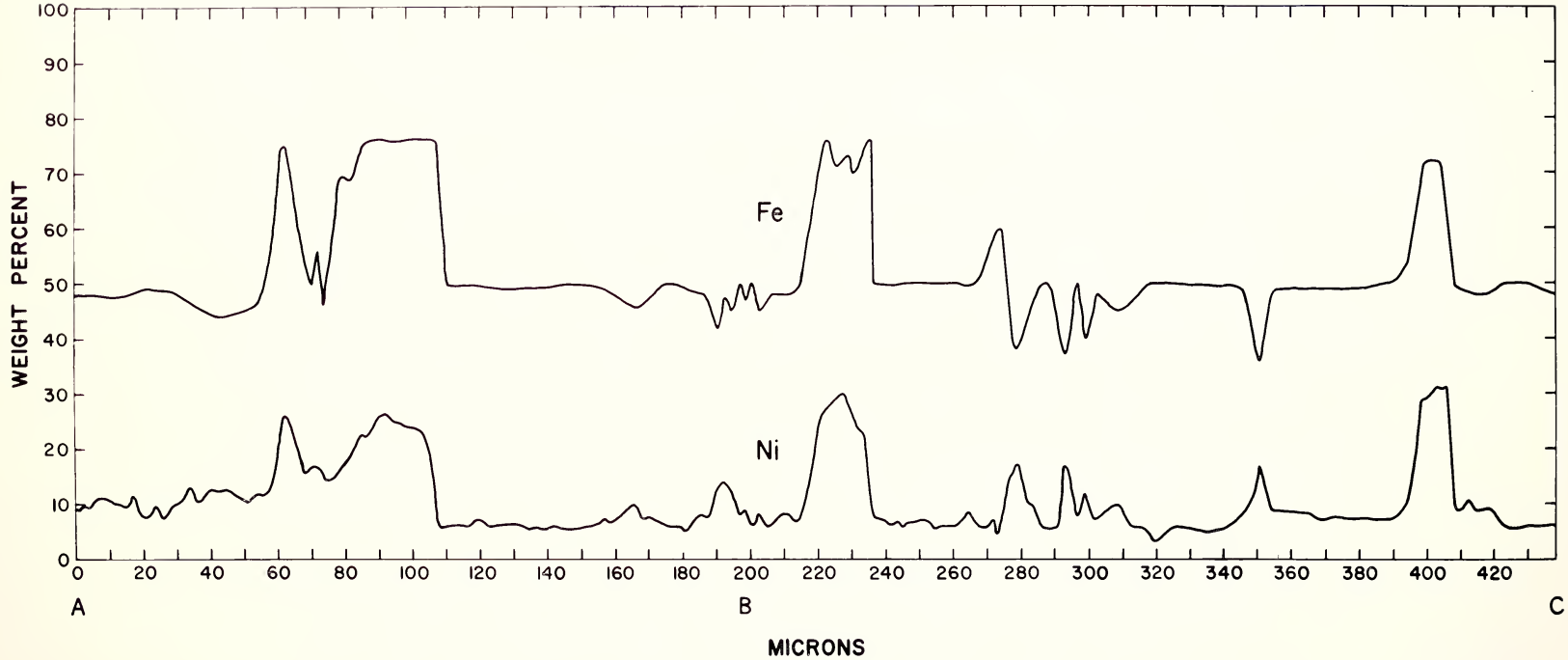

FIG. 21.—34.10. Simultaneous electron microprobe traces across metal-containing area of the broad axe oxide for Fe and Ni (see *fig. 18*). The sample was moved laterally under a 1 micron electron beam at a rate of 8 microns per minute. The four peaks, where the sum of Ni (20–30 percent) and Fe (approx. 75 percent) approaches 100 percent, represent areas of taenite composition. Minor peaks in the Ni trace represent areas of high nickel oxide.

axe, 34.10) containing material of taenite composition shown in *figure 18*. This trace started at A in the photomicrograph and went to B, and then to C after a small change in direction. *Figures 22* and *23* are similar traces made in the indicated areas in *figures 19* and *20*. These tracings show the change in distribution of Ni and Fe as the probe beam moves from oxide, across metal, and then back into oxide.

The Fe and Ni analyses of broad axe (34.10) blade material of taenite composition in Table 4 are confirmed and presented in perhaps a more instructive way in *figure 21*. Four distinct simultaneous peaks in Fe and Ni concentration indicate taenite composition, 70 to 76 percent Fe and 26 to 30 percent Ni (peaks at 60 microns, 85 to 105 microns, 220 to 235 microns and 395 to 405 microns). These values total approximately 100 percent, excellent agreement considering the limitations of this technique. The high Ni peaks appeared on the chart recorder as the electron beam was optically observed to pass from oxide to bright metal. The oxide composition is relatively uniform in most areas, averaging about 6 percent Ni. The sum of Ni and Fe is about what would be expected for a material that is essentially Ni-containing iron oxide. Occasional Ni values in the oxide are as high as 15 percent and correspond generally to lower than average Fe values. This type of variation is not surprising considering the patchy appearance of the oxide. One Fe peak (at 270 microns) is considerably above the average for this element, and it appears to correspond to a slightly lower value for Ni. A possible explanation is the presence of a small amount of material of kamacite composition just below the oxide surface.

Figure 22 presents the results of a simultaneous trace for Ni and Fe across an area containing material of kamacite composition indicated in the photomicrograph (*fig. 19*) of the broad axe (34.10) blade oxide. For convenience of presentation different scales are used to present concentrations of the two different elements. The main difference is that the Ni data are presented in slightly more detail than is the case in *figure 21*. The metal areas in this case contain approximately 7 percent Ni and 92 percent Fe, as would

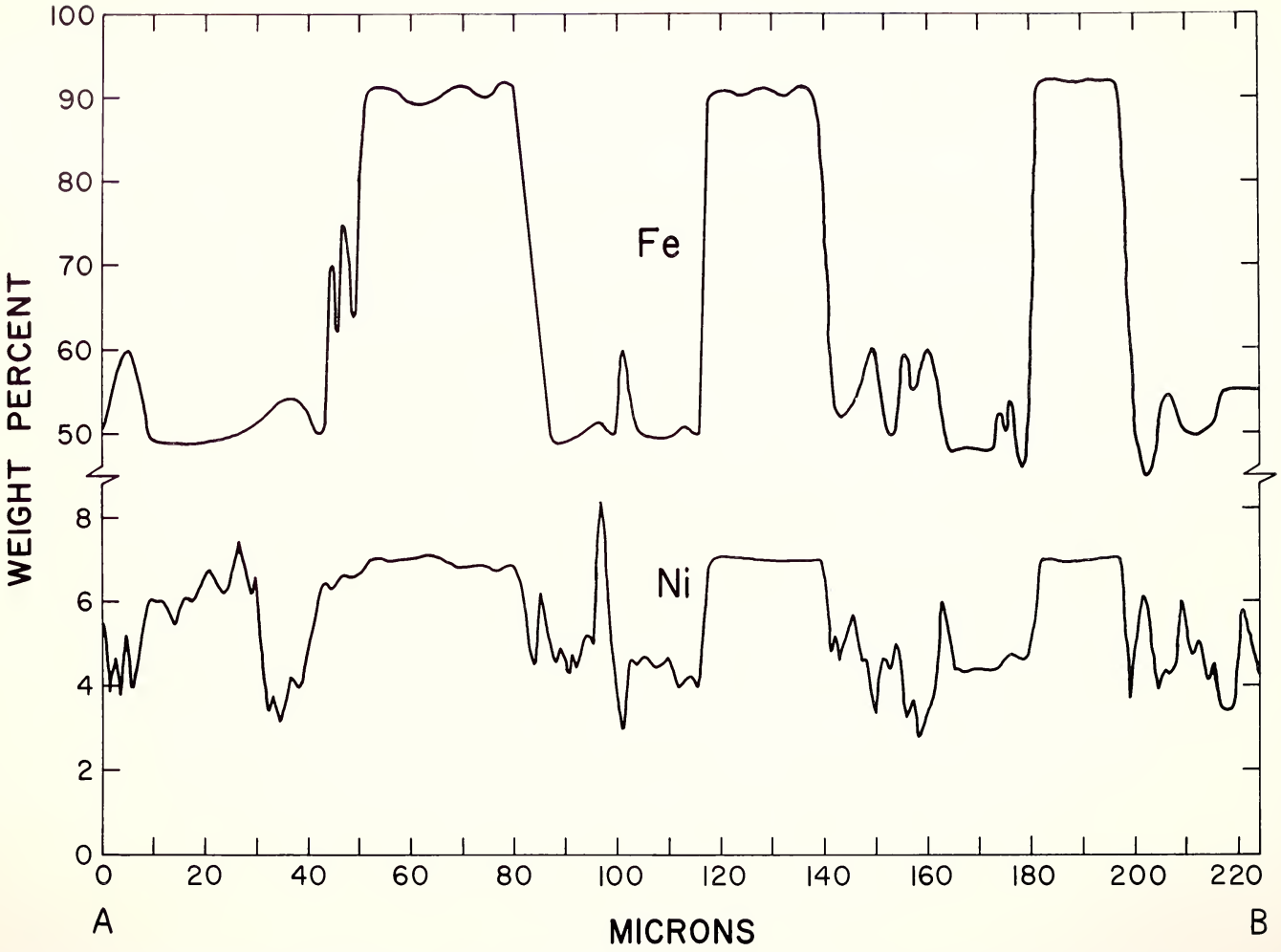

Fig. 22.—34.10. Simultaneous electron microprobe traces across metal-containing areas of broad axe oxide for Fe and Ni (see *fig. 19*). The sample was moved under a 1 micron electron beam at a rate of 8 microns per minute. The three peaks, where the sum of Ni (approx. 7 percent) and Fe (approx. 92 percent) approach 100 percent, represent areas of kamacite composition.

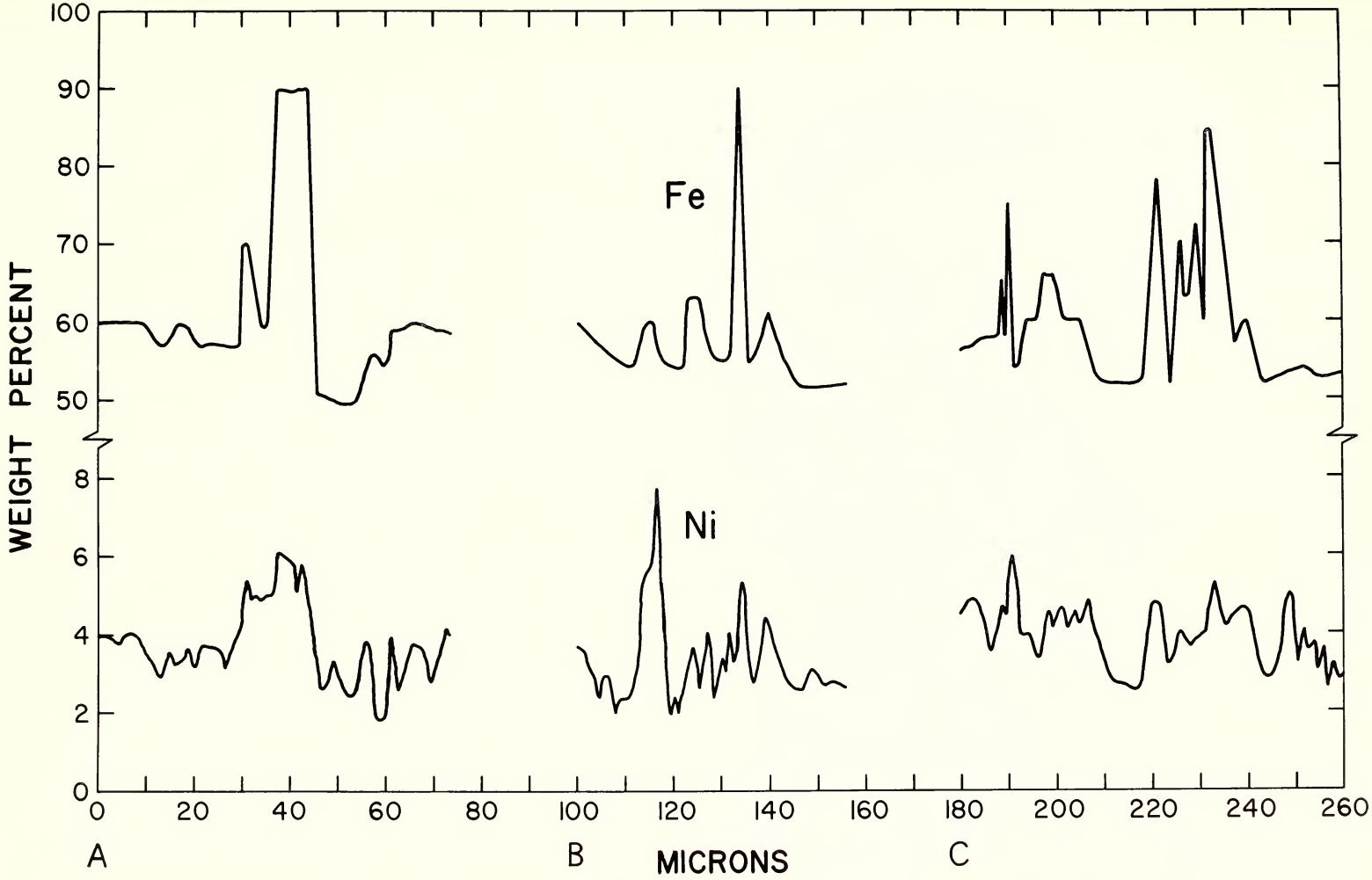

FIG. 23.—34.11. Three separate pairs of simultaneous electron microprobe traces across metal-containing areas of dagger axe oxide for Fe and Ni (see *fig. 20*). The sample was moved under a 1 micron electron beam at a rate of 8 microns per minute. The resolution is poor, but three areas are indicated where the sum of Ni and Fe approaches 100 percent, indicating material of kamacite composition.

be expected from the data in Table 4. The composition of the oxide is similar to that discussed above, with the exception that the average Ni content is probably somewhat lower.

Figure 23 presents the results of three simultaneous traces for Ni and Fe from the areas indicated in *figure 20*, the photomicrograph of the dagger axe (34.11) point oxide. Each of these areas contains a small amount of material that closely approximates kamacite composition and confirms similar data in Table 4. It is obvious that pieces of remnant metal are present only in very small amounts on this surface. The oxide composition is similar to that of the broad axe (34.10) blade material discussed above.

Octahedrite structure and remnant oxide

The analytical and other data reported above is more meaningful when viewed in the context of modern work on the structure of octahedrite meteorites. This background material is important to a valid interpretation of our data. The compositions and remnant structures observed in the case of the broad axe (34.10) blade material are consistent with metallurgically worked meteoritic material followed by weathering during burial.

Iron meteorites are classified on the basis of their crystallographic structure. This structure is displayed when flat, highly polished surfaces are etched with appropriate chemical reagents. Specimens of the largest single group of iron meteorites, called octahedrites, develop a pronounced pattern under these conditions which is referred to as a Widmanstätten pattern after Alois Widmanstätten who observed the phenomenon in 1808. The Widmanstätten pattern of a coarse structured octahedrite meteorite is shown in *figure 24*. This type of pattern, sufficiently coarse to be obvious to the unaided eye, is known only in iron meteorites. Similar patterns have been observed in artificial materials, but they require high magnification to be seen. Excellent reviews of the discovery and early history of the Widmanstätten pattern have been given by Smith (1960, 1962) and Paneth (1960). A general introduction to iron meteorites and their classification has been given

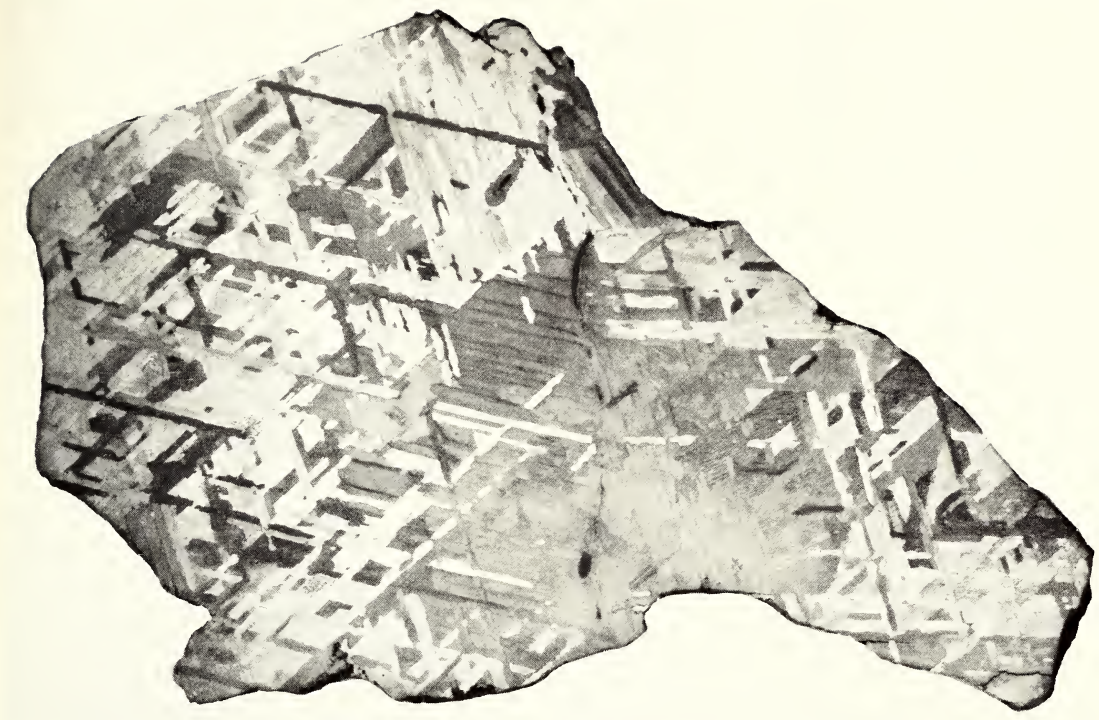

FIG. 24. — Widmanstätten pattern revealed in the Arispe, Mexico, iron meteorite. The lamellae in the photograph are kamacite, their differing reflectivities are caused by differing crystallographic orientations. The kamacite plates are separated by taenite lamellae (see *fig. 26*) that are too fine to be revealed at this low magnification. NMNH 229, polished and etched slice (about × 0.4).

by Mason (1962), and a detailed discussion of their metallography by Perry (1944), Buchwald (1966) and Axon (1968).

The Widmanstätten structure contains important clues for an understanding of the history and origin of iron meteorites, and for this reason has been extensively studied over the years. Recent work relying heavily on modern metallurgical concepts and electron microprobe phase analysis has confirmed and extended earlier ideas based on less detailed data. The broad outlines of the process of Widmanstätten pattern formation are now generally agreed upon. Important recent papers in this field are by Feller-Kniepmeier and Uhlig (1961), Agrell, Long and Ogilvie (1963), Gold-

stein and Ogilvie (1965), Short and Andersen (1965), Reed (1965) and Buchwald (1967).

The observed structure of octahedrite meteorites may best be understood in terms of a slowly cooled Fe-Ni alloy containing at least 6.5 percent Ni. The equilibrium phase relationships involved below 1000° are approximated in *figure 25*. This diagram, taken from Goldstein and Ogilvie (1965), is based on the data of Owen and Liu (1949). It may be used to explain in broad outline the development of the Widmanstätten pattern. An example of this process is an alloy of Fe containing 7 percent Ni which is cooled slowly through the sub-solidus region of taenite stability. Cooling rates of meteorites are slow enough to permit the development of large single crystals of taenite, and this crystal structure controls the subsequent development of the Widmanstätten pattern. At about 750°C the cooling alloy enters the taenite-kamacite region of stability and subsequently kamacite nucleates and grows at the expense of taenite. The transformation of taenite to kamacite is a diffusion-controlled process. The phase relationship is such that as the temperature drops both taenite and kamacite become richer in Ni. Around 450°C the diffusion rate of Ni in Fe becomes so low that the observed Widmanstätten pattern is frozen in. Ni concentration gradients are present in the structure due to arrested diffusion resulting in non-attainment of equilibrium.

Ni gradients are particularly pronounced in taenite at the taenite-kamacite interface (Short and Andersen, 1965). *Figure 26* is a photomicrograph of a small area of Widmanstätten pattern from a sample of the Campo del Cielo, Argentina, meteorite, one of many octahedrite meteorites that could have been selected to make this point (see Cassidy *et al.*, 1965, for an introduction to the Campo del Cielo, Argentina, strewn field and the many meteorite specimens that have been recovered there over a period of nearly 400 years). The light grey matrix is kamacite, and the three parallel lamellae are taenite. The presence of distinct, sharp borders at the taenite-kamacite interface corresponds to high Ni concentration. This photomicrograph is at the same magnification as the oxide photomicrographs shown earlier.

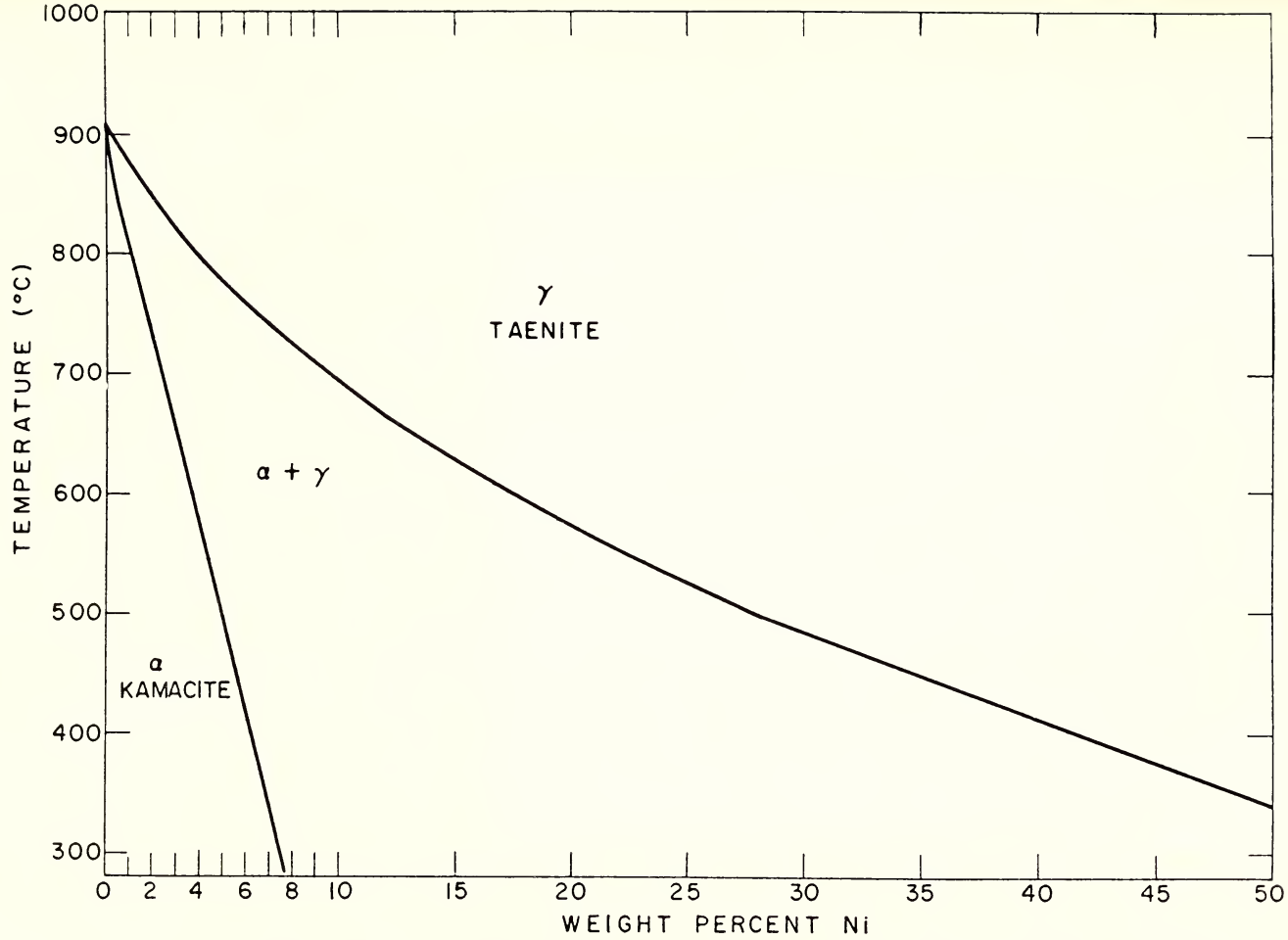

FIG. 25. — The low temperature region of the Fe-Ni equilibrium phase diagram. Areas of this diagram indicate conditions of temperature and Ni concentration where taenite (γ), kamacite (α), and both taenite and kamacite are stable phases. This diagram may be used to interpret the Widmanstätten pattern observed in octahedrite meteorites.

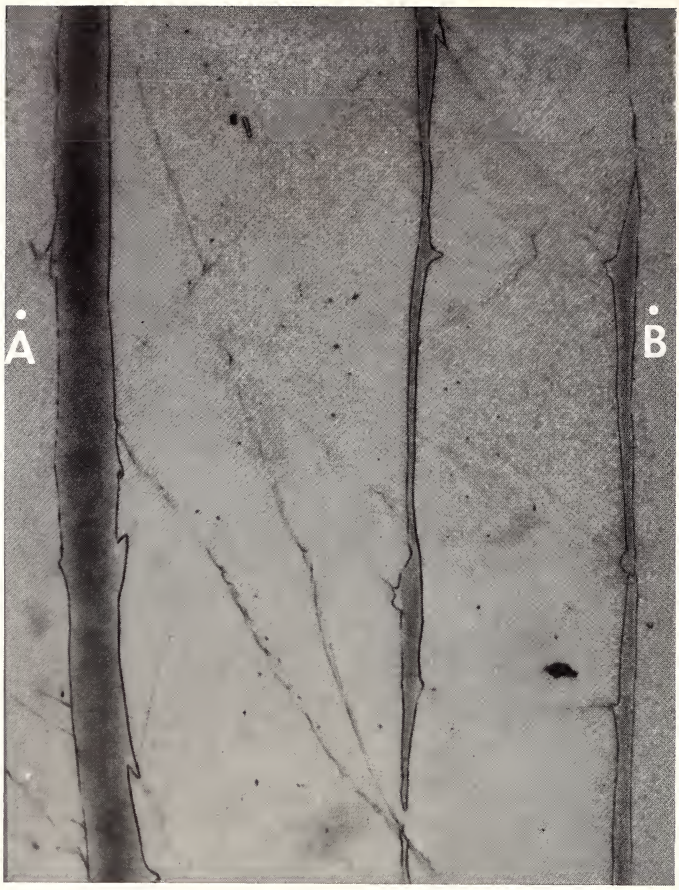

FIG. 26. — Photomicrograph (×230) of a selected area in a section of the Campo del Cielo, Argentina, meteorite (NMNH-2253). The gray background is kamacite, the three vertical lamallae are taenite. The letters A and B indicate the path of the electron microprobe trace in *figure 27*.

Ni and Fe electron microprobe profiles (*fig. 27*) were obtained on the Campo del Cielo section (*fig. 26*) by the same electron microprobe technique used earlier for the weapon oxides. The M-shaped Ni profiles for taenite expected on the basis of careful work by others (for instance, Short and Andersen, 1965) were reproduced in an approximate form. The diffusion gradients at the taenite borders are obvious, although not as sharp and well resolved as would be the case with more painstaking work.

Figure 27 summarizes in a general way the Ni and Fe distribution over a portion of the Widmanstätten pattern of an octahedrite meteorite. The areas of high Ni content are traces across taenite, and the highest Ni values are at the taenite-kamacite borders. The Ni gradient within a given taenite is greater with increasing width of the taenite lamellae. The three taenites shown vary from less than 10 microns to approximately 30 microns in width. These are well within the normal size range for the feature. The bulk of the material represented by the trace in *figure 27* is kamacite. The Ni concentration in kamacite is generally uniform but does decrease measureably near taenite lamellae. For both kamacite and taenite, the Fe distribution varies inversely with Ni. Fe and Ni total approximately 100 percent, a small amount of Co being present in both phases.

Figure 27 may also be used to correlate data from *figures 21* to *23* and to relate these data to measurements made on an unoxidized specimen of the Campo del Cielo meteorite. *Figure 21* is suggestive of *figure 27*, both figures having three restricted areas of high Ni content. These peaks represent the metal areas of *figure 18*, and the Ni and Fe distribution in *figure 21* is roughly that of the known taenite lamellae in *figure 27*. The significant difference between *figures 21* and *27* is the absence of diffusion borders in *figure 21*. Diffusion borders are represented in *figure 27* by the high Ni spikes on either side of the taenite peaks at the kamacite-taenite interfaces. However, the gross composition of the lamellae in our weapon oxide sample, their widths and relative spacing, and their presence in a Ni-containing iron oxide strongly suggest that they are remnant taenite lamellae derived from an octahedrite meteorite.

Figures 22 and *23* contain regions that are similar in composition to the kamacite regions of *figure 27* and to the more accurate analyses reported in Table 4. *Figure 22* contains three areas where both Ni and Fe content is relatively uniform. The Ni is in the 6 to 7 percent range and Fe is 92–93 percent. The small metallic particles analyzed in the areas represented by *figure 23* give the same general picture as that presented in Table 4. The left-hand set of

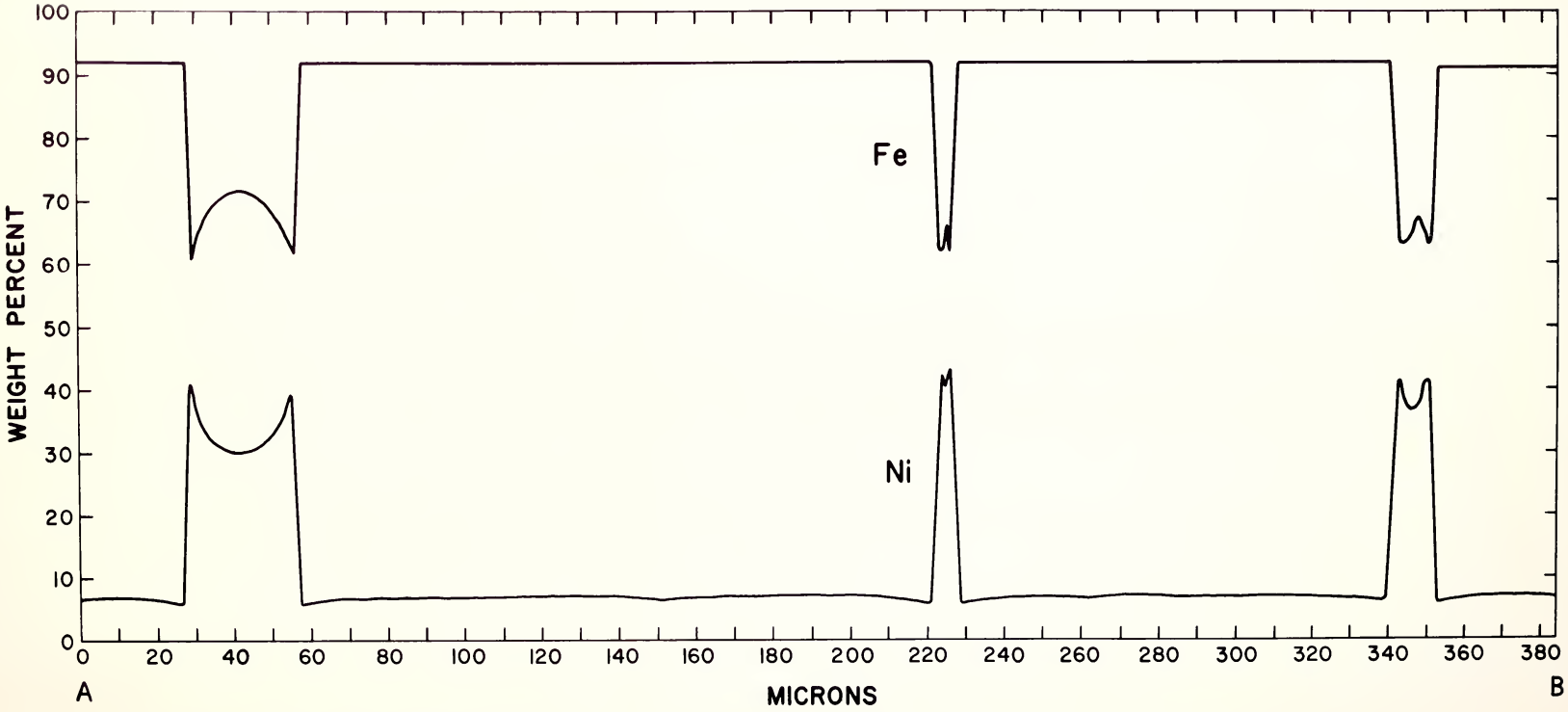

FIG. 27. – Simultaneous electron microprobe traces across the Campo del Cielo meteorite section illustrated in *figure 26*. The sample was moved under a 1 micron beam at a rate of 8 microns per minute. The three peaks represent taenite composition, while the remainder of the trace indicates kamacite.

curves is particularly similar to the data presented in *figure 22*. The high iron peaks in the other two sets of data in *figure 23* suggest kamacite composition. Each is too high for an oxide composition, and is accompanied by an appropriate amount of Ni for kamacite.

Rounding of the apparent taenite peaks in *figure 21* probably requires an explanation other than simply corrosion. Data similar to that presented in *figure 27* was taken from a second Campo del Cielo meteorite specimen. One containing areas of terrestrial weathering was selected, and data was taken over a taenite lamella embedded in oxide. The Ni and Fe distribution curves in the oxide were similar to the oxide curves discussed previously. Within the taenite lamella, however, the Ni diffusion borders were still present. This would seem reasonable on the basis that metal containing the highest Ni would be expected to be the most resistant to weathering.

A reasonable explanation for the lack of diffusion borders would be metallurgical working of the sample. Ramdohr (see above) reported that he found evidence for this in his optical examination of the taenite lamellae. It is well known that heat treatment and working damage the Widmanstätten structure of meteorites. The dissolution of taenite borders is one of the effects noted (Wood, 1964, p. 436). Buchwald (1967) states that "we know now that the diffusion in the metallic matrix is so rapid that significant transformations take place already during short heat-treatments above 500–600 °C." At higher temperatures both kamacite and taenite are brought into the taenite region of the phase diagram (*fig. 25*). On rapid cooling of this material a new phase, $alpha_2$, is formed. It may well be that the materials of kamacite and taenite composition that we are dealing with in this study have undergone a history of heat treatment and mechanical working and have been transformed to the $alpha_2$ phase while maintaining remnant structures and compositions. A history of this type would have a rounding effect on the Ni profile in remnant taenite lamellae. In the discussion of the fabrication of these objects it was pointed out that the bronze members were cast on to

the shaped blades. This technique would have required heating of the iron blades to temperatures above 600 °C for a few minutes.

A further observation that is consistent with a history of marked transformation of meteoritic material was the lack of fine-structure in the metallic particles. Both unaltered meteoritic kamacite and taenite typically contain fine-structure, which develops on etching and is observable under the microscope. The structure within the taenite in *figure 26* is an example of this. An attempt was made to etch the metal remnants in the broad axe (34.10) blade oxide, but no change was observed even with long exposure to a strong Nital etching solution.

Remnant metal in Wolf Creek meteoritic oxide

The literature contains several reports on remnant metallic inclusions in known meteoritic oxide from the large Wolf Creek Crater, Western Australia (Cassidy, 1954). Our interpretation of these data leads us to conclude that this oxide is analogous in important ways to the broad axe and dagger axe oxide we have studied. Wolf Creek meteoritic oxide is relatively abundant and until recently was the only meteoritic material recovered from this locality. La Paz (1954) examined large polished surfaces of two Wolf Creek specimens and reported that the oxide contained "small granules and sinuous veins of metallic nickel-iron." These were clearly revealed although not abundant. White, Henderson and Mason (1967) have also reported sparsely disseminated metallic particles in samples of Wolf Creek oxide. One of these particles was analyzed by the electron microprobe and found to contain 21.3 percent nickel, a value that was attributed to selective enrichment during weathering. The possibility that the particle was remnant taenite, an explanation that seems more plausible, apparently was not considered. Knox (1967) also reports the presence of small metal particles surviving in this material, one of which he identified as kamacite. E. P. Henderson (personal communication, 1968) has examined Wolf Creek oxide and reports finding areas where the oxide structure clearly reveals remnant

Widmanstätten pattern. All of these observations are consistent with derivation of Wolf Creek oxide from an octahedrite meteorite, a meteorite with a Widmanstätten pattern of kamacite and taenite. Furthermore, they support the suggestion by Taylor (1965) that unoxidized octahedrite meteorite specimens found near the Wolf Creek Crater may be part of the crater-forming body. The fragmented nature of the recovered specimens is also suggestive of material found at known octahedrite impact sites such as Barringer Meteor Crater, Arizona; Henbury Craters, Australia; Wabar Craters, Arabia; and Sikhote-Alin Craters, eastern Siberia (Hey, 1966). Another similarity worth noting is that both completely oxidized remnant material and essentially unoxidized specimen material are abundant at Barringer Meteor Crater, Arizona (Nininger, 1956).

Native iron

Iron and nickel-iron are known as rare minerals from a small number of natural occurrences. The iron-bearing basalts of Disko Island, Greenland, are the best-known example (Pauly, 1969). Several reasonably large masses of native iron have been recovered from this area, and iron disseminated in the basaltic matrix is common. The total amount of iron, however, is very small and the geographic area involved limited. This type of iron deposit has never been a major source of the metal, and reports of its use in utensils are doubtful.

Native iron specimens normally contain Ni and small amounts of Co, S, P and C. These are the same elements associated in iron meteorites but there are marked differences in composition, mineralogy and petrography. The Ni in native iron is generally in the 2 percent range and rarely over 3 percent. Native nickel-iron specimens containing major quantities of Ni are also known, their Ni contents normally ranging above 60 percent. Terrestrial iron or nickel-iron is essentially unknown in the composition range of kamacite and taenite from iron meteorites. The Widmanstätten pattern of iron meteorites, with its intimate association of kama-

cite and taenite, has not been reliably demonstrated in terrestrial irons and probably does not exist there. Native iron structures and mineral associations are more suggestive of white cast iron and slags than they are of meteorites. It is highly unlikely that native irons were used to manufacture the blades of the weapons that produced the remnant oxide studied here.

Meteoritic origin of remnant oxides

The data in the preceding sections allow us to conclude that the iron blades associated with these bronze objects were fabricated from meteoritic iron. Undoubtedly, the meteoritic structures originally present were damaged both in fabrication of the blade and in the casting of the bronze tangs. The two blades may have come from different iron meteorites, the data being ambiguous on this point. In any event, the objects had sufficiently different weathering histories, undoubtedly as a result of conditions during burial, to produce remnant oxides of markedly different character. The broad axe (34.10) blade oxide developed under sufficiently reducing conditions to produce a corrosion product largely of magnetite and therefore to maintain the bulk of the Ni originally present. The dagger axe (34.11) point oxide was formed under more oxidizing conditions and a limonitic oxide developed, most of the original Ni being lost. Remnant structures observable in the oxide of the broad axe (34.10) blade and the presence of material of kamacite and taenite composition strongly suggest that this oxide was derived from an octahedrite meteorite, a meteorite showing a definite Widmanstätten pattern. The presence of metal of kamacite composition in the dagger axe (34.11) oxide is evidence for weathering of an iron meteorite. In this case, however, neither structural nor compositional data sufficient to establish the structural class of the meteorite was developed. We find much in our data to support the general thesis of a meteorite being the source of the iron and nothing that is inconsistent with it.

V. SIGNIFICANCE OF THE FINDINGS

What significance do our findings have in the context of the metalworking technology of early Chou China? We have proven to the limits of our present ability the hypothesis of the meteoritic origin of the iron in these objects, and we have also advanced evidence for casting-on joining in these two weapons. For these facts to be relevant, they must be related to other iron, bronze and composite objects both from China and from other cultures. Before these relationships can be pointed out, we must place the weapons in their correct chronological and geographical locations.

With the two weapons came a statement in Chinese by Ch'u Tê-i which has been translated as follows (Freer Gallery of Art, 1946, p. 91):

> "Twelve bronze weapons of the Chou dynasty. In the 6th moon of the 20th year of the Republic of China [1931] a native dug up in Wei-hui-fu, Honan Province, not far from An-yang District, a group of ancient weapons, namely: six halberds [*ko*], one lance [*mou*], two hatchets [*fu*], and three knives [*tao*]. On one of the knives are the two characters K'ang Hou [Marquis K'ang]. K'ang-shu was a younger brother of King Ch'êng of Chou, and his appanage included what are now An-yang District and Wei-hui Prefecture. [K'ang-shu was actually Ch'eng Wang's uncle, as pointed out in footnote 12 a, *ibid.*] These 12 weapons are undoubtedly relics of the Chou Marquis K'ang. Among them is a *Ch'ih-yu* knife, a circular knife, an ox-head halberd and a halberd inlaid with shell. Antiquities so remarkable in form and make have not been seen hitherto. By students of the manners and customs of ancient Chou, they must be regarded as great treasures. Recorded by Ch'u Tê-i. The 11th day of the 10th moon of the 20th year of the Republic of China [1931]."

Mr. Lodge commented as follows:

> "Ch'u Tê-i is said to have been associated in some capacity with the famous collections gathered and published by the late

Tuan Fang. In any case, his record of these weapons is at present our only available information as to where and when they were found, and there is no apparent reason to doubt its essential accuracy. Just how Ch'u groups the weapons as *ko*, *mou*, and *fu* is not clear in every case; but those he describes as 'a Ch'ih-yu knife' (34.3), 'a circular knife' (34.4), 'an ox-head Halberd' (34.7), 'a halberd inlaid with shell' (34.8), are all easily identifiable."

To recapitulate, Ch'u says that these weapons were included in a group of twelve found together in the ground by a native (probably a farmer) in June, 1931. He says that the find occurred near An-yang in the Wei-hui prefecture of the Province of Honan. (A year later, controlled excavations started near this area, at a place called Hsin-ts'un.) While this information does not have the authority of a report from a controlled excavation, it does seem to be accurate. Ch'u Tê-i, as implied in Mr. Lodge's comments above, had a great deal of experience with ancient Chinese bronzes, and he wrote the C. T. Loo Catalogue of 1924 along with other books on Chinese antiquities (Ta T'ang, 1962).

On the other hand, Ch'u's statement is not without ambiguity. We must remember that this information accompanied the weapons when they were purchased and must have added to their market value; the statement also consists of hearsay evidence at best. What can we find to confirm the assertions set forth by Ch'u?

Clandestine digging is known to have been in progress in the area of the Hsin-ts'un cemetery and at other locations within the boundaries of the old Wei state during 1931, the date that Ch'u assigns to the finding of these weapons. "Before 1932 the region [Hsin-ts'un] was a happy hunting ground for curio-diggers. Plundering was going on with great enthusiasm in the spring of 1931 when the provincial government prohibited digging, after which official excavations were carried out for four successive seasons in 1932–33" (Cheng, p. 76). A group of eight objects in the Royal Ontario Museum is said to have come from Hsin-ts'un by way of

FIG. 28. — Set of bronze weapons, early Chou dynasty, owned by the Freer Gallery of Art. Much reduced in scale.

the art market; one *chi* (R. O. M. number NB. 3155) is inscribed with the character for *Hou* or marquis. W. C. White says (1956, p. 164) that when objects started to be unearthed at Hsin-ts'un in the spring of 1931, "At once dealers from the port cities swarmed to the area, paying exhorbitant prices for anything they could lay their hands on . . . ." The demand thus created would have encouraged further clandestine digging, and the rapid movement of these objects onto the art market would have further obscured the exact facts of any particular case.

The connection of our weapons with other objects may be the surest way of confirming Ch'u's statement. We have attempted below to draw parallels for our *ko* and *chi* weapons with those excavated by Kuo Pao-chün at Hsin-ts'un, Hsün Hsien. Ch'en Meng-chia (1948 and 1955) groups our large *tao* together with 7 other weapons and vessels, including the Malcolm *kuei* (see below). All of these bear a *K'ang-hou* inscription. He says that this set was probably found together, in the same pit, at the same time, but it is clear that his reason for grouping them together is the inscription. He does not, therefore, mention the uninscribed weapons that we possess. Ch'en also states the following: that the objects were not all made at the same time; that the Malcolm *kuei* was probably made by a Shang craftsman; and that the location of the finding of the set is not precisely known. He mentions three alternative possibilities for the provenance: Wei-hui-fu (modern Chi Hsien), Chün Hsien (or Hsün Hsien), and Ku-yü-ts'un in Hui Hsien. All three lie within a fifty-mile radius to the south of An-yang. While Ch'en does not advance actual evidence for any of the three, he believes that the Hui Hsien site is the most probable. Because of the clandestine nature of the finding of these objects and the intervening years, we do not think that we can do more than accept what Ch'u says, and assume that these weapons were found near Wei-hui-fu. At least we can be fairly sure that they were found within the territory ruled by Marquis K'ang, Duke of Wei. The assertion that they were all found together also stands, there being no evidence to the contrary. We can infer that they were also buried together.

TABLE 5b

Spectrographic analyses of the set of bronze weapons.†

Bi %	Zn %	Cr %	Mg %	As %	Mn %	Si %	Ca %	Al %	FGA No.
.2	nd	<.001	<.001	.03	<.001	.02	.1	.001	34.3
nd	nd	nd	.0005	.01	.0005	.03	.005	<.0005	34.4
.06	nd	nd	.001	.1	.0005	.03	.003	<.0005	34.5
nd	nd	<.001	<.001	.03	<.001	.001	nd	.001	34.6
.03	nd	nd	.001	.2	.0005	.005	.0007	<.0005	34.7
.005	nd	nd	.0007	.1	.0005	.0005	<.0005	<.0005	34.8
nd	nd	nd	.0007	.1	.0005	.001	.005	<.0005	34.9
—	nd	<.001	<.001	nd	nd	0.01 to 0.1	—	nd	34.10

TABLE 5a

Wet chemical analyses of the set of bronze weapons.*

FGA No.	type‡	place sampled	Cu %	Sn %	Pb %	Fe %	Zn %	Total %	Date Analyst Size of samples
34.3	*tao*	handle	83.66§ 82.98 83.4	13.48 14.52 14.0	0.0 0.0 0.0	— — —	— — —	97.4	6/18/62 EWF 80 mg.
34.4	*ch'i*	bottom	79.64 83.37 81.5	17.16 16.17 16.7	0.0 0.15 0.1	0.0 0.0 0.0	0.0 0.0 0.0	98.3	5/26/69 IVB 56 mg.
34.5	*ko*	hafting ridge	87.20 87.34 87.3	10.92 11.37 11.2	0.47 0.46 0.5	0.0 0.0 0.0	0.0 0.0 0.0	99.0	6/2/69 IVB 56 mg.
34.6	*tao*	bottom	85.80 86.54 86.2	11.10 11.64 11.4	0.0 0.0 0.0	— — —	— — —	97.6	6/18/62 EWF 100 mg.
34.7	*ko*	top of tang	87.24 87.10 87.2	6.15 6.00 6.1	4.14 4.60 4.4	0.0 0.0 0.0	0.0 0.0 0.0	97.7	5/28/69 IVB 56 mg.
34.8	*ko*	top of haft	83.07 83.07 83.1	14.87 14.59 14.7	1.98 1.98 1.98	0.0 0.0 0.0	0.0 0.0 0.0	99.8	6/3/69 IVB 56 mg.
34.9	*ko*	break in blade	85.80 85.67 85.7	12.99 12.69 12.8	0.0 0.15 0.1	0.0 0.0 0.0	0.0 0.0 0.0	98.6	5/22/69 IVB 56 mg.
34.10	*ch'i*	tang	81.91 81.77 81.8	15.78 15.71 15.8	tr. tr. tr.	— — —	— — —	97.6	12/22/60 EWF 75 mg.

TABLE 5b

Spectrographic analyses of the set of bronze weapons.†

FGA No.	Au %	Pb %	Ag %	Fe %	Co %	Ni %	Sb %	Bi %	Zn %	Cr %	Mg %	As %	Mn %	Si %	Ca %	Al %	FGA No.
34.3	—	.03	.03	.009	.009	.03	.01	.2	nd	<.001	<.001	.03	<.001	.02	.1	.001	34.3
34.4	nd	.01	.01	.04	.005	.001	.001	nd	nd	nd	.0005	.01	.0005	.03	.005	<.0005	34.4
34.5	<.005	.02	.08	.06	.007	.06	.01	.06	nd	nd	.001	.1	.0005	.03	.003	<.0005	34.5
34.6	—	.03	.09	.1	.009	.07	.01	nd	nd	<.001	<.001	.03	<.001	.001	nd	.001	34.6
34.7	.005	.8	.05	.01	.007	.03	.15	.03	nd	nd	.001	.2	.0005	.005	.0007	<.0005	34.7
34.8	<.005	.6	.05	.06	.007	.005	.02	.005	nd	nd	.0007	.1	.0005	.0005	<.0005	<.0005	34.8
34.9	<.005	.005	.01	.01	.007	.03	.04	nd	nd	nd	.0007	.1	.0005	.001	.005	<.0005	34.9
34.10	—	0.01 to 0.1	0.001 to 0.01	0.01 to 0.1	0.001 to 0.01	0.01 to 0.1	0.01 to 0.1	—	nd	<.001	<.001	nd	nd	0.01 to 0.1	—	nd	34.10

TABLE 5a continued

FGA No.	type	place sampled	Cu %	Sn %	Pb %	Fe %	Zn %	Total %	Date Analyst Size of samples
			81.85	14.55	0.0	—	—		4/14/64
34.10	*ch'i*	back of	81.55	14.60	0.0	—	—		IVB
		blade	81.7	14.6	0.0	—	—	96.3	100 mg.
			86.34	12.03	2.05	—	—		12/22/60
34.11	*ko*	tang	84.55	12.36	2.19	—	—		EWF
			85.4	12.2	2.2	—	—	99.8	80 mg.
	small	top	—	—	—	—	—		6/3/69
34.12	blade	back of	85.47	10.2	2.07	—	—		IVB
		blade	85.5	10.2	2.1	—	—	97.8	50 mg.
			90.28	7.25	0.92	0.0	0.0		5/27/69
34.13	blade	top of	90.31	7.50	0.91	0.0	0.0		IVB
		blade	90.3	7.4	0.9	0.0	0.0	98.6	56 mg.
			85.69	12.94	0.31	0.0	0.0		6/20/69
34.14	*chi*	bottom	85.88	12.78	0.15	0.0	0.0		IVB
			85.8	12.9	0.2	0.0	0.0	98.9	56 mg.

TABLE 5b continued

FGA No.	Au %	Pb %	Ag %	Fe %	Co %	Ni %	Sb %	Bi %	Zn %	Cr %	Mg %	As %	Mn %	Si %	Ca %	Al %	FGA No.
34.10	<.005	.01	.001	.001	.005	.005	.001	nd	nd	nd	.0007	.01	.0005	.0005	.0005	<.0005	34.10
34.11	—	—	0.1 to 1.0	0.01 to 0.1	0.01 to 0.1	0.01 to 0.1	0.01 to 0.1	—	nd	<.001	<.001	0.1 to 1.0	nd	0.001 to 0.01	—	0.1 to 1.0	34.11
34.12	<.005	.45	.05	.005	.005	.01	.02	nd	nd	nd	.003	.08	.0005	.01	.01	.001	34.12
34.13	.005	.35	.02	.06	.005	.03	.04	nd	nd	nd	.03	.15	.001	.3	<.0005	<.0005	34.13
34.14	nd	.22	.16	.05	.002	.01	.22	.07	nd	—	—	.22	—	—	—	—	34.14

Notes to tables 5a and 5b:

* The wet analyses were done by the same method as those in Gettens, 1969 (ch.III). EWF = Elisabeth West FitzHugh. IVB = Ilona V. Bene.

† Since the spectrographic analyses were done at different times and places and with different experimental conditions, they are included here simply for interest and not for precise use; therefore, dates, sample sizes, etc. have been left out of table 5b (see also Gettens, 1969, table IB). The analyses of 34.4, 34.5, 34.7, 34.8, 34.9, 34.10 (back of blade), 34.12 and 34.13 were all run by Harold Westley of the C.A.L., U.S.N.M., in July, 1970.

‡ The type names used here are taken from the old Freer bronze catalogue (Freer Gallery of Art, 1946).

§ In all cases except for 34.12, the analyses consist of two duplicate analyses and an average. The sample taken was split into two portions, visible contamination and corrosion products picked out under a binocular microscope, and two duplicate analyses run. In all cases, the average has been rounded to one figure beyond the decimal point. In the case of 34.12, only one analysis was available, so this is given again as the average.

TABLE 5b continued

Zn %	Cr %	Mg %	As %	Mn %	Si %	Ca %	Al %	FGA No.
nd	nd	.0007	.01	.0005	.0005	.0005	<.0005	34.10
nd	<.001	<.001	0.1 to 1.0	nd	0.001 to 0.01	—	0.1 to 1.0	34.11
nd	nd	.003	.08	.0005	.01	.01	.001	34.12
nd	nd	.03	.15	.001	.3	<.0005	<.0005	34.13
nd	—	—	.22	—	—	—	—	34.14

Viewing these weapons as a group, however, it does not seem likely that they were made simultaneously or in the same workshop (*fig. 28*). The chemical analyses of these weapons make this idea even more believable (Tables 5 a and 5 b). Take for instance the blade, or as Loehr (1956, p. 8) calls it, a socketed axe, 34.13. This contains more Cu than any of the others in the group, some Sn, and a little Pb, and the analysis differs greatly from any of the other weapons. On the other hand, weapons which we would think of as typically Hsin-ts'un forms such as 34.5, 34.7, and 34.14 contain about 86 to 87 percent Cu; 34.5 and 34.14 are very similar in their analyses, containing 11 or 12 percent of Sn and a little Pb, while 34.7 has much higher Pb content than these two. The analyses of 34.10 and 34.11 do differ to some extent. At this stage it is difficult to attribute these differences to their actual causes; the weapons may have come from different workshops, different ores may have been used, a development of technique may have taken place in a single workshop, or the bronze foundry practice may have been sufficiently non-uniform to show these variations as a consequence. Some technical analyses of other material from the same site (now at the Academia Sinica on Taiwan) might shed some light on this matter. We hope that this table can serve as a base for consideration of other early Chou bronze weapons, but we cannot draw any definite conclusions from it at this stage.

The typological viewpoint promises to be of more help. Judging from the different styles of *ko* represented in this collection, one may assume that the weapons were made at different times or in different workshops. (Compare 34.5, 34.8, 34.9, 34.7, and 34.11 in *fig. 28*; see also the old Freer Catalogue, pl. 48 and 49.)

Sinologists do not yet agree on the typological evolution of the *ko*. The most intensive study of the typology of the *ko* was written by James Menzies, but he only follows the evolution of the *ko* down to the end of the Shang dynasty. Li Chi has also studied the *ko* in detail. Magdalene von Dewall has traced the evolution of the *ko* at the Hsin-ts'un site. She remarks that our set contains

FIG. 29 a. — Broken blade of the type *ch'i*, FGA 34.14. Length, 21.3 cm.

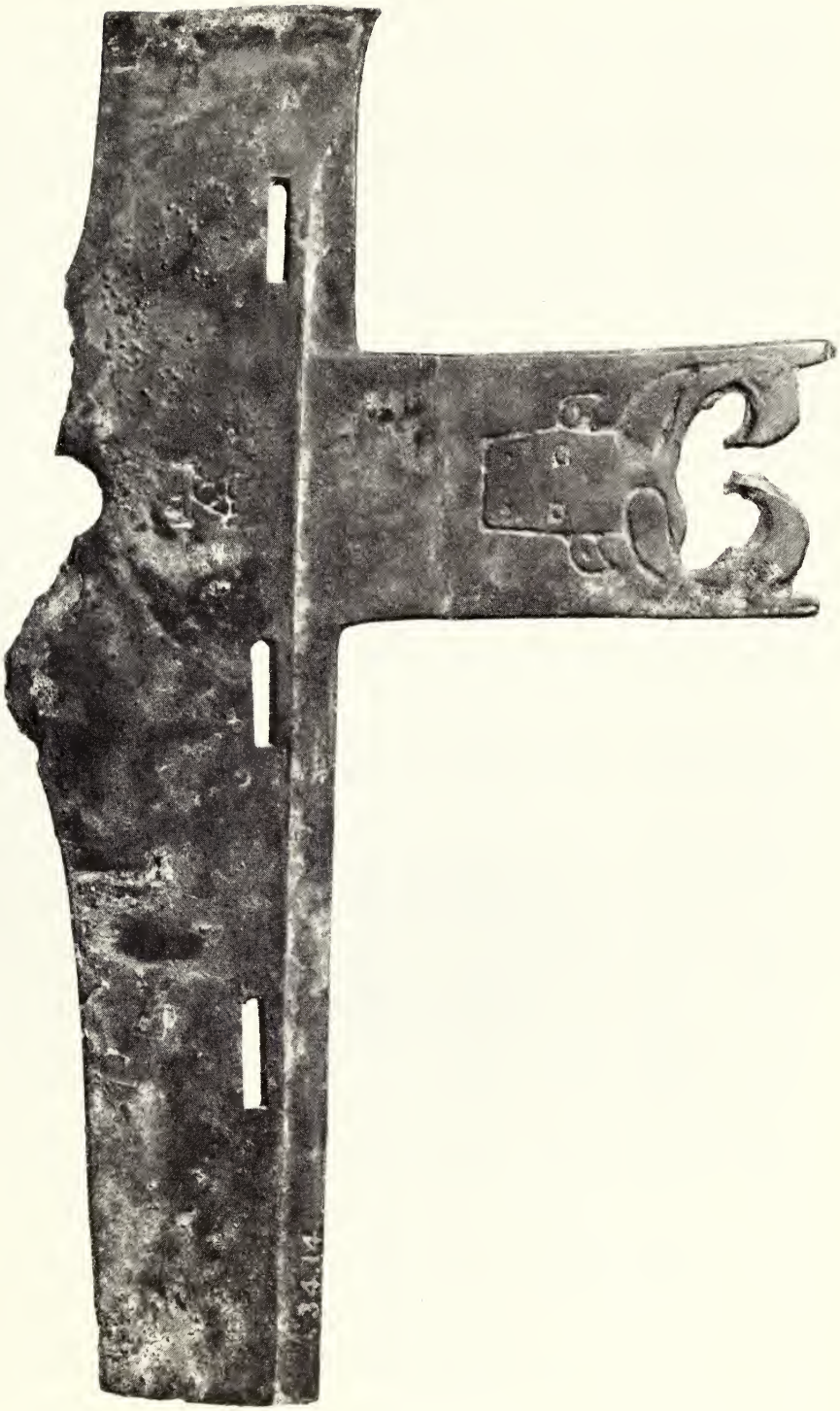

Fig. 29 b. — Broken blade of the type *ch'i*, FGA 34.14.

ko which can be classed under Li Chi's class PV (34.11 – the iron-bronze *ko*), PVI (34.7, 34.8, 34.9) and the intermediate form between PVII and PVIII. From the inscription *"K'ang hou"* on the large slashing knife or *tao*, she links our set with other inscribed objects from this cemetery, and she concludes:

> "It is clear that both phases must have been so close in time that the same historical personage could be mentioned, to wit as contemporary, in both instances. The span of two successive generations is thus, indeed, the longest period for which this fact makes allowance. In terms of historical chronology, this span must have covered the era immediately following the Chou conquest, dominated by the strife for military and political consideration in which the Prince of Wei is known to have taken an active part" (p. 527).

It seems that these weapons might have come from the tomb of the Prince of Wei which must have been in the Hsün Hsien area and was looted. This possibility appears even more probable when we consider that many of these weapons have correspondences in the scientifically excavated material. Compare, for example, our 34.7 with M 42 : 103 (Kuo, 1964, pl. XVIII no. 15) and our 34.8 with M 42 : 14 (Kuo, 1964, pl. XIX no. 13). The larger and more ornate weapons which do not correspond to the excavated material add weight to the hypothesis of princely ownership of these weapons.

A hitherto unpublished weapon from this group contributes further evidence to the argument. It is a thinly-patinated blade of the type *chi* (our 34.14), with both the top, back-curving portion and the blade broken off (*fig. 29a* and *b*). A perforation appears where the base of the blade would be, as on M 42 : 108 (Kuo, 1964, pl. XXIII no. 1) and the lashing holes appear in the same places as they do on M 42 : 102 (Kuo, 1964, pl. XXIII no. 2, pl. LXVIII no. 1). We originally thought that this object might be spurious, but it is too close to the excavated material in style to discard as a fake, and its chemical composition also fits in closely with the rest of our group. The inscription also has some interesting features visible even to a non-epigrapher. One character appears on

the side which shows when the blade points to the left. This might possibly be a corruption of *hou* as written on the Freer *tao* (Freer Gallery of Art, 1946, p. 94). On the other side of the blade four characters appear. These might read "heaven king's son" with the fourth character uncertain. This formula could apply to Marquis K'ang, the Prince of Wei, since he was the brother of King Wu. The elucidation of this inscription and in fact a detailed discussion of all of the weapons must wait for a qualified epigrapher to consider the problem.

A surprisingly large amount of material exists for this study. For instance, the Malcolm *Kuei* described by Yetts (1937) and Ch'en (1948 and 1955) contains an inscription which mentions Marquis K'ang. The script style is very similar to that on our *tao* 34.6. The *kuei* also has a well-preserved surface, bronze in color, similar to the silvery surface on some of our weapons, especially 34.3 and 34.4. A weapon mentioned by Loehr (1956, no. 105) is of the same type as our 34.6 and is also inscribed. Loehr connects this with our t*ao*, but considers that it is a Shang prototype of our weapon.

Of greatest interest to the historian is the presence of textual evidence for the existence of Marquis K'ang. This evidence is dealt with by Yetts and Ch'en in some detail. K'ang is the recipient of "the announcement to the Prince of K'ang" in the *Shu ching* (Legge, vol. III, p. 381ff.). Here the Duke of Chou speaks as Regent with the authority of King Ch'êng and charges K'ang with the careful and conscientious management of the area which previously contained the Shang capital. It is of more interest to us that K'ang, later Marquis Wei, was also present at King Ch'êng's funeral in 1004 B.C. (Loehr, 1968, pp. 14 and 17), and heard "the testamentary charge" (*Shu ching*, book XXII; Legge, vol. III, p. 544ff.). From this funeral we can derive some idea of what the funeral of Marquis K'ang himself must have been like.

> "The salvage men set out the screens ornamented with figures of axes, and the tents. Between the window and the door, facing the south, they placed the different mats of bamboo basket-work, with their striped borders of white and black

silk; and the usual bench and adorned with different-colored gems. In the side space on the west, facing the east, they placed the different rush mats, with their variegated border; and the usual bench adorned with veined tortoise-shell. In the side space on the east, facing the west, they put the different mats of fine grass, with their border of painted silk; and the usual bench carved and adorned with gems. Before the western side-chamber, facing the south, they placed the different mats of fine bamboo, with their dark mixed border; and the usual lacquered bench.

"They set forth also the five kinds of gems, and the precious things of display. There were the red knife, the great lessons, the large convex symbol of gem, and the rounded and pointed maces....

"Two men in brownish leather caps, and holding three-cornered halberds, stood inside the gate leading to the private apartments: Four men in caps of spotted deer-skin, holding spears with upturned blades, stood one on each side of the steps east and west, and near to the platform of the hall. One man in a great officer's cap, and holding an axe, stood in the hall near the front at the east end. One man in a great officer's cap, and holding a somewhat different axe, stood in the hall, near the front at the west end. One man in a great officer's cap, and holding a lance, stood at the front and eastern end of the hall. One man, in a great officer's cap, and holding a somewhat different lance, stood at the front and western end of the hall. One man in a great officer's cap, and holding a pointed weapon, stood by the steps on the north."

Here are mentioned many weapons, of different shapes, some similar to those in the Freer Gallery. In any case, we can confidently attribute our weapons to within a couple of generations of the Chou conquest, which would make their date 1000 B.C. plus or minus about 50 years, depending on which of the various chronological schemes one adopts. They very probably come from the Hsin-ts'un site, and possibly from the tomb of Marquis K'ang.

The *ch'i* broad axe (34.10), however, is clearly a hold-over from the Shang dynasty. Cheng Te-k'un (p. 242) points out that 34.10 is the only example of this type of weapon to be recovered from an early Chou context, and that this is a characteristically Shang weapon type. In considering similar examples, Loehr tentatively dates them Shang and definitely dates number 6 in the Jannings catalogue as Shang (pp. 20, 121, pl. V). These axes all have an asymmetrical tang, a *t'ao-t'ieh* on the tang and another on the blade, and a hole in the position of the mouth of the lower *t'ao-t'ieh*. So, our axe might be a Shang artifact or the translation of a Shang type into this early Chou context.

The *ko* dagger axe 34.11, also bears affinities to Shang types, and while von Dewall classes it as a PV *ko*, the definite lack of a down-turning flange on the bottom of the blade seems to imply affinity to the PIII class, a class that belonged primarily to the Shang period but lingered into the Chou at Hsin-ts'un. It may be that the theory of a period of Shang-Chou transition when the Chou people were producing weapons and vessels modeled on Shang prototypes but with a definite Chou flavor is the correct explanation of the appearance of some of these weapons (Loehr, 1968, p. 96; this idea was set forth in greater detail in an unpublished lecture by Virginia Kane "Bronze Vessels of the Shang-Chou Transition"). We must wait, however, for a complete technical, stylistic, and epigraphical study of this group of weapons to be made before the whole story can be told.

How does the use of iron in 34.10 and 34.11 relate to Chinese iron-casting technology? The easiest answer would be, "not at all." These two weapons are isolated instances of the use of iron as an ornamental device, just as jade was used in Shang times. The iron here appears as the blade, as does jade in the Freer *ko* 41.5 and the axe or implement 41.4 (Freer Gallery of Art, 1946, pl. 43). This is entirely unlike the later use of iron for arrow shafts and agricultural implements. In fact, later in China, bronze was considered "the lovely metal" and iron "the ugly metal" (Needham, p. 2). While iron was also used for sumptuary arts, especially in belt-hooks, its major use was for ploughshares, tools, and so

forth. Kwang-chih Chang thinks that iron metallurgy in China probably dates from late in the period of the Spring and Autumn Annals (possibly around 600 B.C.) and the industry was in full swing in the early Warring states period (Chang, 1968, p. 313). This certainly corresponds with the archaeological evidence, and places our two weapons about 400 years before the wide industrial use of iron in China, clearly an anomalous position.

Of course, as a number of writers make clear (see Needham, Chang Kwang-chih and Von der Merwe), the iron technology of early China is based on cast iron, and not wrought iron or steel. Needham states that "in the occidental world, the true iron age did not begin until about 1200 B.C., although terrestrial iron has been occasionally worked by man since a date of the order of 2700 B.C." This places the beginning of the iron age in the occident at a time contemporary with the Shang dynasty in China. Iron appears in India around 800 B.C. (Banerjee, p. 239). So these weapons occur at a time before the introduction of iron foundries in China and India, and since there appears to have been no connection between the Near East and China, at least as far as the introduction of iron casting is concerned, these weapons are unique instances of the early use of iron in China, probably from a meteoritic source. These weapons must also have been unique in their own time, fit for a prince.

There are many mentions of meteorite falls in ancient Chinese literature (Chang, *Lapidarium Sinicum,* p. 372–384). Most of these are simply stories of meteor sightings and their interpretations as portents. If the metal in these weapons had been seen to fall from the sky it would certainly have been interpreted as auspicious and this might be one reason for its use in the place of jade in these weapons. Such a use of meteoritic iron might also explain the fact that only one iron meteorite find is known from China.

Of course, meteoritic iron, while rare, is by no means unknown to archaeology. The people of other cultures are known to have employed meteoritic iron to manufacture utensils and objects of adornment even when they lived generally on a stone-age

level. The Eskimos of Northern Greenland fabricated harpoon-heads and scraping knives by hammering meteorite fragments and inserting them into bone handles (Buchwald and Munch, 1965, p. 11 and figures 1–7). Several instances are known of fabrication of plough-shares, machetes and nails of iron meteorites found by the native Mexican Indians and mestizos. The Hopewell Indians of North America are known to have made many objects of meteoritic iron, probably from the Brenham pallasite transported from Kiowa County, Kansas (Wasson and Sedwick, 1969). The pioneers of 19th century North America often forged implements of local meteoritic iron (Buchwald, 1965). It appears, in fact, that about 10 percent of all known iron meteorites have been wholly or partly heat-treated by man in attempts to split and utilize the material (V. F. Buchwald, personal communication). A detailed discussion of the history of many iron meteorites is in preparation by Buchwald.

Many summaries of the use of meteorites by primitive man have appeared (Zimmer, 1916; Richardson, 1934; Partington, 1935; and Pokrzywnicki 1960/61). In these the emphasis is on weapons, but Richardson also mentions manufacture of amulets, beads, rings, and images. Smith (1965) points out that early man used new materials with their esthetic possibilities foremost in his mind. "For his delight man tries many things: for utility he employs only what he knows will work."

The final question that arises is the use of the casting-on technique in the fabrication of these weapons. European metalworkers used this technique frequently in early periods (Drescher, 1958, pl. 15). In China, the technique was also used in bronze vessel production even before the period of these weapons. A *tsun* in the Freer collection (51.19) has animal-head decor which was apparently cast first and the vessel then cast on to it. A *hu* (49.5) has flanges which were inserted into the mold and the vessel was then cast on to them (Pope *et al.*, 1967, pp. 102 and 43). This technique continues into the Chou period, as can be seen on a *yu* (30.26, *ibid.*, p. 355). It is interesting that the blades of these two weapons are cast on differently. That of 34.11 is chamfered like an arrow-

head, but that of 34.10 is drilled to provide recesses for inflow of molten bronze.

Both methods apparently gave a sure attachment. The Chou artisan was accustomed to working with the casting-on technique and it must have seemed the natural method to use in this instance.

A close examination of these two objects of the material culture of ancient China has proved very instructive. We have been able to describe them in detail, to ascertain how they were made, and to relate them to their archaeological context. The proof of the use of meteoritic iron in these objects indicates the sensitivity of the ancient Chinese craftsman to materials, and in particular to the use of what must have been to him, a new and different material. Holding these aged, damaged and corroded objects in our hands, we appreciate the delight Marquis K'ang must have taken in owning them; and the establishment of this direct, tangible link to the mind of a man who lived three thousand years ago is one of the greatest pleasures an investigator can have.

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